The behaviour of parent and daughter nuclides in aerosols released in radiological dispersion events: a study of a SrTiO3 source

V. R. van Maris, a,b C. M. Naji, b F. G. Di Lemma, a,b J.-Y. Colle, b* D. Bykov a and R. J. M. Konings a,b

During rapid high-temperature events, like a terrorist attack with radiological dispersal device, radiological material will be released into the environment. In these scenarios, the ratio between parent and daughter nuclides can be used for nuclear forensic investigations to determine the age of the used radioactive source. We have used fast laser heating to produce aerosols of a material often found in radioisotope thermoelectric generators. To investigate the behaviour of SrTiO3, we have recreated pure and mixed samples, mimicking several parent-to-daughter ratios. By combining scanning electron microscopy and energy-dispersive X-ray spectroscopy analysis with Raman spectroscopy, we were able to distinguish different elements and phases present in the aerosols. Two types of aerosols have been identified: individual aerosols from a few micrometre to a few tens of micrometre and agglomerates of smaller aerosols from a few hundred nanometre to a few micrometre. The bigger aerosols, formed from mechanically expelled liquefied material, showed a parent-to-daughter ratio that stays close to the value that would be anticipated by the initial composition of the material, but in the agglomerates, formed from vaporised material, the presence of the daughter elements reduces significantly due to differences in the condensation behaviour.

Introduction

Radioactive sources can be misused to create a radiological dispersal device (RDD) (a.k.a. ‘dirty bomb’). The source material is dispersed during a rapid high-temperature event with a considerable possibility that radiological material will be released into the environment. A likely material that could be used for this is Strontium-90 (90Sr), which was used in the form of SrTiO3 as a fuel for radioisotope thermoelectric generators (RTGs) that use the heat of radioactive decay to generate electricity. In the past, RTGs were used at remote monitoring sites and unmanned lighthouses and are currently still being used in space applications. Some of these terrestrial RTGs have not been decommissioned yet, and those located at unmanned sites are vulnerable for theft and misuse, because they are guarded with limited security measures.

Radioactive materials can damage human tissue through external radiation or internal radiation upon inhalation or ingestion. The risk of inhaling radioactive particles related to such a detonation depends on the aerodynamic equivalent diameter (AED) of the aerosols. Particles that can be inhaled are required to have an AED < 10 μm, and those that are smaller than AED < 0.1 μm will even be likely to be absorbed into the bloodstream upon inhalation. Additionally, recent studies show that also the crystalline form influences the cytotoxicity. For instance, in the case of TiO2, rutile nanoparticles induce toxic effects, while anatase nanoparticles do not.

Many studies were performed to understand the consequences of radiological dispersion events (RDEs). Different computational models have been used to study dispersion effects. However, because the smallest motions in the atmosphere are hard to predict but still influence the outcome, results from these models are always a compromise between completeness and time frames.

Explosion experiments have been conducted to research aerosol types and sizes. The results are used to determine the extend of the exclusion zone that should be evacuated in case of a RDD detonation and to determine the perimeters that have to be decontaminated before daily life can be resumed. Various authors report that two different aerosol morphologies are created in these events, which are the result of different formation processes. It is suggested that the larger spherical particles, with an AED of a few micrometre, originate from the liquefied material and are expelled by the mechanical shock. Smaller particles, with an AED between ten to a few hundred nanometre,
are formed by rapid condensation of the vapour and are generally observed as agglomerates.

When time passes, the radioactive inventory of the source changes, strontium-90 ($^{90}$Sr) decays into yttrium-90 ($^{90}$Y) and subsequently into zirconium-90 ($^{90}$Zr). Because the half-life of $^{90}$Sr and $^{90}$Y is known, the amount of each material can be calculated for any time after the production of the source and, therefore, also the ratio between parent and daughter nuclides. In nuclear forensics, this ratio is often used to determine the date of production.

The current research is, in particular, intended to find out whether the ratio between parent and daughter nuclides of the radioactive source materials remains unchanged in aerosols formed after the rapid high-temperature event. For instance, one can imagine that the elements behave differently and the partition over different aerosol size affects the ratio between parent and daughter nuclides. To do so, we have produced aerosols from recreated pure and mixed samples to mimic the parent to daughter ratios. The combination of multiple techniques, mainly scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and Raman spectroscopy enable us to gain information on the aerosols size, composition and stable phase formed during such an event.

Materials and methods

The radiological dispersion events setup

To create the aerosols in a rapid high-temperature event, similar to those of a RDD, the radiological dispersion events setup (RADES) has been used. The RADES has been described extensively and is capable of rapidly increasing the temperature of a small sample by means of a laser pulse. Contrary to those experiments, where the laser power is controlled by a PID controller, in these experiments, the laser power is set at a fixed value and turned on for a predefined period of time.

![Figure 1](image_url). A scheme of the inside of the micro-orifice uniform deposit impactor (MOUDI). [Colour figure can be viewed at wileyonlinelibrary.com]

### Table 1. Nominal cutoff sizes for each stage.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Nominal cutoff size μm</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
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<td>7</td>
<td>0.32</td>
</tr>
<tr>
<td>8</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The aerosol collection system is a MSP Micro-Orifice Uniform Deposit Impactor (MOUDI) model 110R-MRD371, which consists in this setup of nine impactor plates (numbered from 0 to 8) on which the aerosols are collected (Fig. 1). These stages are designed in such a way that when an airflow of 30 L/min is maintained, the probability that a particle with an AED of the nominal cutoff size will impact on this plate exceeds 50%. The nominal cutoff size for each stage is given in Table 1. More information on how this MOUDI works can be found in the reference.

### Samples

Although it is intended to describe the behaviour of radioactive elements, for simplicity reasons, we decided to use the stable isotopes of the relevant elements, as the isotopic composition will not influence the chemical behaviour.

The decay of $^{90}$Sr occurs with a half-life of $T_{1/2} = 28.64$ years, while the half-life of $^{90}$Y is much shorter: $T_{1/2} = 64.1$ h. So depending on the production date, the source will contain only small amounts of $^{90}$Y that decays to the stable $^{90}$Zr. Both decays occur through beta emission. Very little structural damage is produced by the beta decay. The recoil energy of the $^{90}$Sr and of the $^{90}$Y atoms is lower than the threshold displacement energy. Thus, the beta decay of $^{90}$Sr into $^{90}$Zr is unable to generate defects.

At room temperature, SrTiO$_3$ has a perovskite cubic structure (space group $Pm3m$) where Sr, Ti and O occupy respectively the 1a, 1b and 3c sites. Upon $^{90}$Sr nuclear decay, $^{90}$Y and $^{90}$Zr are supposed to occupy the same cationic site (1a). It is shown that cubic perovskite SrTiO$_3$ can accommodate only up to 8 mol% of Y in the 1a site. For higher Y concentrations, a two-phase mixture was obtained with mainly SrTiO$_3$ and $Y_2$Ti$_2$O$_7$. Similarly, it is shown that cubic perovskite zirconium titanite is unstable, and it optimises its geometry by changing into the orthorhombic scutnityte structure.

In order to investigate the behaviour of these materials, we have performed our experiments on four sets of compounds grouped in Table 2.

**Pure titanates**

The first group contains the ‘pure titanate’ compounds. Experiments were performed with SrTiO$_3$, $Y_2$Ti$_2$O$_7$ and ZrTiO$_4$ separately, in order to achieve a deep understanding of their individual behaviour. SrTiO$_3$ and $Y_2$Ti$_2$O$_7$ were obtained by mixing stoichiometric amounts of SrCO$_3$, $Y_2$O$_3$ and TiO$_2$ anatase reagents of high purity in a Retsch Mixer Mill MM400. The materials were mixed for at least 6 h in a stainless steel jar with a zirconium inner coating and a zirconium ball in the vibrational mill. Afterwards, the powders were pressed into pellets at a pressure of 7 tonnes or
Because it is reported that strontium was mainly used in RTGs, [1]
ternary mixtures given in the third group containing ‘binary’ compounds.

Any phenomena of interaction between those elements; these are
50% of the ‘pure titanate’ compounds to determine if there are
Further experiments were done with the three combinations of
Binary mixtures were produced from this material.

Ternary mixtures

Because it is reported that strontium was mainly used in RTGs,[11]
which were in mass production between 1976 and 1990, two samples
were made that would represent an age of 38 and 24 years
old; these can be found in the fourth group: the ‘ternary’ mix-
tures. Attempts to obtain a single phase of compounds described
in the second group indicates the percentage of yttrium in the sample. The num-
erber 50 in the third group indicates that these samples are a 50% mixture, and the
numbers in the first and fourth group indicate different samples.

Yttrium-doped strontium titanates

The second group contains (Sr1−xYx)TiO3 with x = 0.01, 0.02,
0.04 and 0.08, the ‘yttrium-doped strontium titanate’ compounds.
These compounds were synthesised by the same process as the
‘pure titanate’ compounds. Sample SY1, which is mentioned in
Table 2, was only used as a reagent for later samples; no aerosols
were produced from this material.

Binary mixtures

Further experiments were done with the three combinations of
50% of the ‘pure titanate’ compounds to determine if there are
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tures. Attempts to obtain a single phase of compounds described
in the groups with binary and ternary mixtures have failed.
Therefore, stoichiometric amounts of SrTiO3, Y2Ti2O7, ZrTiO4 and
(Sr1−xYx)TiO3 in powder form were intimately mixed to get a good
homogeneity and pressed with an hydraulic press into pellets
of 5 mm in diameter and a few millimetres in height. No further
heat treatment was performed. An overview of the investigated
samples is presented in Table 2.

Table 2. Details of the samples that were used in this research

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample composition</th>
<th>Origin</th>
<th>Known impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>SrTiO3</td>
<td>synthesised</td>
<td>10% (ZrO2)</td>
</tr>
<tr>
<td>Y1</td>
<td>Y2Ti2O7</td>
<td>synthesised</td>
<td>5% (TiO2)</td>
</tr>
<tr>
<td>Z1</td>
<td>ZrTiO4</td>
<td>commercial</td>
<td>1%</td>
</tr>
<tr>
<td>SY1</td>
<td>(Sr0.99Y0.01)TiO3</td>
<td>synthesised</td>
<td>1%</td>
</tr>
<tr>
<td>SY2</td>
<td>(Sr0.98Y0.02)TiO3</td>
<td>synthesised</td>
<td>1%</td>
</tr>
<tr>
<td>SY4</td>
<td>(Sr0.96Y0.04)TiO3</td>
<td>synthesised</td>
<td>1%</td>
</tr>
<tr>
<td>SY8</td>
<td>(Sr0.98Y0.02)TiO3</td>
<td>synthesised</td>
<td>5% (Y2Ti2O7)</td>
</tr>
<tr>
<td>SY50</td>
<td>50% SrTiO3 + 50% Y2Ti2O7</td>
<td>mixed</td>
<td></td>
</tr>
<tr>
<td>SZ50</td>
<td>50% SrTiO3 + 50% ZrTiO4</td>
<td>mixed</td>
<td></td>
</tr>
<tr>
<td>YZ50</td>
<td>50% Y2Ti2O7 + 50%ZrTiO4</td>
<td>mixed</td>
<td></td>
</tr>
<tr>
<td>SYZ1</td>
<td>40% (Sr0.99Y0.01)TiO3 + 60%ZrTiO4</td>
<td>mixed</td>
<td></td>
</tr>
<tr>
<td>SYZ2</td>
<td>54% (Sr0.99Y0.01)TiO3 + 46%ZrTiO4</td>
<td>mixed</td>
<td></td>
</tr>
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</table>

All samples contain titanium and oxide. The sample names containing the letter ‘S’ contain strontium, ‘Y’ contain yttrium and ‘Z’ contain zirconium. The number in the second group indicates the percentage of yttrium in the sample. The number 50 in the third group indicates that these samples are a 50% mixture, and the numbers in the first and fourth group indicate different samples.

68.5 kN for approximately 5 min. Heat treatment was applied for
at least 15 h in a Borel Special Furnace TL 1100-8 at 1000°C. This
procedure has already been described previously.[16] ZrTiO4 was
obtained commercially.

Yttrium-doped strontium titanates

The second group contains (Sr1−xYx)TiO3 with x = 0.01, 0.02,
0.04 and 0.08, the ‘yttrium-doped strontium titanate’ compounds.
These compounds were synthesised by the same process as the
‘pure titanate’ compounds. Sample SY1, which is mentioned in
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Binary mixtures

Further experiments were done with the three combinations of
50% of the ‘pure titanate’ compounds to determine if there are
any phenomena of interaction between those elements; these are
given in the third group containing ‘binary’ compounds.

Ternary mixtures

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homogeneity and pressed with an hydraulic press into pellets
of 5 mm in diameter and a few millimetres in height. No further
heat treatment was performed. An overview of the investigated
samples is presented in Table 2.

Analytical equipment

X-Ray Diffraction

X-Ray Diffraction (XRD) measurements were performed using a
PANalytical X’Pert Pro diffractometer with Cu-Kα radiation. The patterns were scanned through steps of 0.008 2θ, between 10
and 80 2θ, with a total measuring time per sample of 40 min.
Purity of the samples was checked by phase analysis with the
HighScore program by implemented matching procedure.

Scanning electron microscopy and energy-dispersive X-ray spec-
troscopy

After the aerosols are created by the laser pulse and collected by
the impactor plates on aluminium sheets, a small piece of approxi-
mately 12 mm in diameter was cut from each sheet and examined
by SEM and Raman spectroscopy. SEM images, both secondary
electron as well as backscatter electron, have been made using a
Philips XL 40 SEM. This machine is also used to perform EDX anal-
ysis; the elemental compositions are obtained by averaging EDX
measurements for each stage.

Raman spectroscopy

Raman analysis of the aerosols deposited on the aluminium
sheets was performed using a Horiba Jobin Yvon T64000 spec-
trometer in the simple monochromator mode. The aerosols were
irradiated using an Ar+ coherent continuous wave laser emitting
at 514.5 nm and x50 long-focal distance objective. The power
impinging the sample surface was below 3 mW. The scattered
light was filtered using a 514.5-nm edge filter, dispersed using a
1800-gr/mm diffraction grating and focussed on a LN2-cooled
CCD detector. The laser spot size is around 2 μm².

Sample characteristics after synthesis

X-Ray Diffraction

The XRD pattern of sample Y1 (Y2Ti2O7) shows some extra peaks
attributed to the TiO2 phase (< 5% as mentioned in Table 2). All
the yttrium-doped strontium titanate samples shows the same
features as the pure cubic SrTiO3. For the composition with 8% Y
(sample SY8), extra peaks attributed to Y2Ti2O7 were identified.
Raman spectroscopy

The Raman spectra of the samples after the synthesis, but before the rapid high-temperature event, are shown together with the spectra of the aerosols that are created in the rapid high-temperature event (See Section on Phase Identification of Aerosols: Raman Spectroscopy). In order to compare these spectra amongst themselves, the spectra of the initial materials are also shown, sorted by the four groups (as defined in Table 2), in Fig. S1 to S4.

Pure titanate group

At ambient temperature and pressure, SrTiO₃ has a centro-symmetric space group. The five atoms in the primitive unit cell are located around an inversion centre. At the Brillouin zone centre, the 15 degrees of freedom lead to

\[ \Gamma = F_{1u}(\text{acoustic}) + 3 \cdot F_{1u}(\text{optic}) + F_{2g}(\text{optic}) \]  

(1)

Because all the zone-centre optical modes are of odd parity, no first-order Raman scattering is expected to occur. However in Fig. S1 (Supporting Information), broad peaks are seen between 240 and 420 cm⁻¹ and between 605 and 730 cm⁻¹ involving the combination of two phonons (a second-order Raman process).[17,18] Y₂Ti₂O₇ has a cubic pyrochlore structure with a Fd³m space group. Factor group analysis for this compound suggests six Raman active modes (A₁g, E₂g and F₂g) and seven infrared active modes (F₁u):

\[ \Gamma = 7 \cdot F_{1u} + A_{1g} + E_{2g} + 4 \cdot F_{2g} \]  

(2)

The wavenumbers of these vibrational modes in the Y₂Ti₂O₇ sample are in very good agreement with those reported in literature.[19] The spectrum (Fig. S1 (Supporting Information)) exhibits four characteristic peaks at 304 (F₂g), 445 (F₂g), 520 (A₁g) and 607 cm⁻¹ (F₂g).

ZrTiO₄ has an orthorhombic α-PbO₂ structure with Pbcn space group. The normal vibration modes, as obtained by factor group analysis, suggest 18 Raman-active non-degenerate modes that can be written using the following irreducible representations:

\[ \Gamma = 4 \cdot A_{2g} + 5 \cdot B_{1g} + 4 \cdot B_{2g} + 5 \cdot B_{3g} \]  

(3)

The main Raman peaks are observed at 160, 256, 408, 641 and 800 cm⁻¹ (Fig. S1 (Supporting Information)). The wavenumbers of these vibrational modes are in very good agreement with those assigned in literature.[20] Except for the mode at 800 cm⁻¹ that was assigned to A₂ symmetry,[21] a complete assignment of these modes is still unknown.

Yttrium-doped strontium titanate group

Raman spectra of the solid solutions ((Sr₁₋ₓYₓ)TiO₃ with x = 0.02, 0.04 and 0.08) shows the same Raman features as SrTiO₃, with an interesting behaviour of the broad bands (Fig. S2 (Supporting Information)). These bands generally tend to narrow and slightly down shift when increasing the Y content, most likely because of the expansion of the lattice and the decrease of the static disorder. However, neither extra peaks of TiO₂ nor of Y₂Ti₂O₇ were observed in the Raman spectra of Y₁ (Fig. S1 (Supporting Information)) and SY8 (Fig. S2 (Supporting Information)), respectively. It is very likely that the Raman cross section of the Ti-O and Y-O vibration in these compounds is very low compared with SrTiO₃ and (Sr₁₋ₓYₓ)TiO₃.

Binary group

The 50% mixed samples (Fig. S3 (Supporting Information)) show mixed Raman features of the individual ‘pure titanate’ materials. Peaks at 304 and at 520 cm⁻¹ are obviously assigned to Y₂Ti₂O₇ compound, while those at 605 and 730 cm⁻¹ correspond to SrTiO₃.

Ternary group

Finally, samples SYZ1 and SYZ2 with all three elements (Fig. S4 (Supporting Information)) resemble ZrTiO₄ the most. The dominance of the ZrTiO₄ Raman features in the mixed compounds SYZ1 and SYZ2 is mainly due to the high Raman cross section of this material.

Overall, it can be concluded that the synthesised samples reveal limited amounts of impurity according to XRD analysis and the Raman spectra obtained shows great resemblance with spectra found in literature. The synthesis process can be considered to be performed successfully.

Results

Morphology of aerosols: SEM images

Previous observations describe two types of aerosol morphologies created in RDE, which are a result of different processes.[6,7,10] The larger spherical particles, with an AED of a few micrometre

Figure 2. Scanning electron microscopy images: large individual particles can be found on the upper stages, stages where aerosols with a bigger aerodynamic equivalent diameter are found. (a) Sample SZ50, stage 1, secondary electron (SE) detector. (b) Sample YZ50, stage 0, SE detector.
Behaviour of parent and daughter nuclides in aerosols formed from SrTiO3 source

Figure 3. Scanning electron microscopy images: cubical crystallization in large individual particles. (a) Sample SY2, stage 1, secondary electron (SE) detector. (b) Sample SY2, stage 1, backscatter electron detector.

Figure 4. Scanning electron microscopy images: small particles that form small agglomerates. (a) Sample SYZ2, stage 5, secondary electron (SE) detector. (b) Sample SYZ2, stage 5, backscatter electron detector.

Figure 5. Scanning electron microscopy images: small particles that form one big agglomerate, showing similarity with a hill made out of grains of sand. (a) Sample SZ50, stage 7, secondary electron (SE) detector. (b) Sample SZ50, stage 7, backscatter electron detector.

(Fig 2), originate from the liquefied material and are expelled by the mechanical shock. The acquired SEM images of the aerosols in this experiment show similar morphologies as the aerosols in the SrTiO3 experiments conducted earlier.\textsuperscript{[10]}

Some of the individual aerosols revealed a crystalline substructure different from the majority of the aerosols; an example is given in Fig. 3. It shows crystallization within the aerosol, where the crystals seem to be cubic and randomly orientated in the aerosol. This crystallization in the aerosols was only found in samples in stage 1, which suggest a relation to the crystallization from the liquid phase.

Smaller particles, with an AED between ten to a few hundred nanometre, are formed by the rapid condensation of the vapour and are generally observed as agglomerates (Figs 4 and 5). Table 3 gives an overview of the distribution of individual particles ('I') and agglomerates ('A').
Table 3. An overview of the stages of the different materials with the indication if individual particles ('I') and/or agglomerates ('A') are recognised on the scanning electron microscopy images.

<table>
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<th>Stage</th>
<th>S1</th>
<th>S2</th>
<th>S4</th>
<th>Z1</th>
<th>Z2</th>
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<th>S25</th>
<th>SY2</th>
<th>SY4</th>
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(a) Sample S1 is marked with ○, sample Y1 is marked with △ and sample Z1 is marked with □. Dotted line indicates expected value for all elements at 50%.

(b) Sample SY50 is marked with ○, sample SZ50 is marked with △ and sample YZ50 is marked with □. Upper dotted line indicates expected value for Ti at 50%. Lower dotted line indicates expected value for Sr, Y and Zr at 25%.

(c) Ratio between parent and daughter nuclides. Dotted lines indicate expected ratios, 0.7956 for SYZ1 and 1.5189 for SYZ2.

Figure 6. Energy-dispersive X-ray data. The dotted lines indicate the expected values. (a) Sample S1 is marked with ○, sample Y1 is marked with △ and sample Z1 is marked with □. Dotted line indicates expected value for all elements at 50%. (b) Sample SY50 is marked with ○, sample SZ50 is marked with △ and sample YZ50 is marked with □. Dotted line indicates expected value for all elements at 50%. (c) Ratio between parent and daughter nuclides. Dotted lines indicate expected ratios, 0.7956 for SYZ1 and 1.5189 for SYZ2. [Colour figure can be viewed at wileyonlinelibrary.com]
Elementary composition of aerosols: EDX analysis

As described in Section on Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy, EDX analysis was performed to analyse the elemental composition as a function of the particle size of the aerosols and thus identify if partitioning of the parent and daughter nuclides occurs. Some stages contained only few aerosols; therefore, the localisation of the aerosols on the impactor plates was a time-consuming process, and especially for the upper stages, it was sometimes difficult just to find a single aerosol. For that reason, for some stages, the EDX measurements could have only been done at few positions. This results in fluctuating average values and large standard deviations for some of the stages. Nevertheless, a clear trend has been found in the EDX results, which is presented in Fig. 6.

Pure titanate group

Figure 6(a) shows the elemental composition of SrTiO₃, Y₂Ti₂O₇ and ZrTiO₄. For SrTiO₃ (sample S1) the percentage of Sr and Ti stays more or less in the range of the expected value (50% for all samples), but for Y₂Ti₂O₇ (sample Y1) and for ZrTiO₄ (sample Z1) the percentage of Y or Zr decreases and the percentage of Ti becomes higher when the particles become smaller.

Figure 7. Raman spectra of aerosols (part 1). Aerosols on different stages and the initial powder (Init. Pow.) before aerosol creation of samples (a) S1, (b) Y1 and (c) Z1. [Colour figure can be viewed at wileyonlinelibrary.com]

Figure 8. Raman spectra of aerosols (part 2). Aerosols on different stages and the initial powder (Init. Pow.) before aerosol creation of samples (a) SY2, (b) SY4 and (c) SY8. [Colour figure can be viewed at wileyonlinelibrary.com]
Figure 9. Raman spectra of aerosols (part 3). Aerosols on different stages and the initial powder (Init. Pow.) before aerosol creation, of sample SY50.

(a) Aerosols on different stages and the initial powder (Init. Pow.) before aerosol creation, of sample SZ50.

(b) Aerosols on different stages and the initial powder (Init. Pow.) before aerosol creation, of sample YZ50.

Figure 10. Raman spectra of aerosols (part 4). Aerosols on different stages and the initial powder (Init. Pow.) before aerosol creation of samples (a) SYZ1 and (b) SYZ2. [Colour figure can be viewed at wileyonlinelibrary.com]

(a) Aerosols on different stages and the initial powder (Init. Pow.) before aerosol creation, of sample SYZ1.

(b) Aerosols on different stages and the initial powder (Init. Pow.) before aerosol creation, of sample SYZ2.

Phase identification of aerosols: Raman spectroscopy

The Raman spectra of the aerosols collected on the stages are presented in Figs 7–10. For comparison, the bottom spectrum in every figure represents the Raman spectrum of the material (in powder form) before the rapid high-temperature event.

Pure titanate group

The Raman spectra of the aerosols produced from SrTiO₃ does not correspond to that of SrTiO₃ before the experiments. There are peaks present around 170, 545 and 790 cm⁻¹, as can be seen in Fig 7(a). The EDX results give no indication for other elements to be present in the aerosols.

By comparing this spectrum to the Raman spectra of SrTiO₃ published in literature, it can be seen that these modes correspond to the first-order phonon vibrations observed at approximately 180, 540 and 780 cm⁻¹ attributed to TO₂, TO₃ and LO₄ modes, respectively. As discussed previously, the room temperature Raman spectrum of SrTiO₃ is dominated by second-order Raman scattering. However, Raman scattering of SrTiO₃ has shown that first-order Raman scattering modes can actually be observed when the local symmetry is broken because of various factors, such as strain effects, the presence of impurities or defects and oxygen vacancies. For nanoparticles of SrTiO₃,
In accordance with EDX results, it is very likely that the percentage of Y present in the aerosols, the continuous back-Raman scattering of few modes through a charge transferring process and the freezing of the rutile phase. Here, we suggest that the presence of the rutile phase is very likely due to the rapid quenching of this high-temperature-stable phase. Few studies show that the presence of a suitable doping agent strongly affects the kinetics of this process. Indeed, some metal species can occupy interstitial positions or induce structural changes in metal oxide structures, as is the case of Nb, V, and Ce loaded onto TiO$_2$.[28] In accordance with EDX results, it is very likely that the presence of Y or Zr in TiO$_2$ aerosols affects the kinetic of this process and the freezing of the rutile phase.

Yttrium-doped strontium titanate group

The Raman spectrum of the aerosols obtained from SY2, SY4 and SY8 are comparable with the Raman spectrum of SrTiO$_3$ (sample S1). It is important to note that we observed a slight change in the shape of the continuous background and the intensity ratio of few bands (especially for the band centred at 520 cm$^{-1}$ relative to the band at 545 cm$^{-1}$). This is very likely due to an electronic process during the Raman measurements. The aerosols were measured on aluminium substrate that can enhance the electronic process during the Raman measurements. The aerosols ratio of few bands (especially for the band centred at 520 cm$^{-1}$) are comparable with the Raman spectrum of SrTiO$_3$ (sample S1). It is important to note that we observed a slight change in the shape of the continuous background and the intensity ratio of few bands (especially for the band centred at 520 cm$^{-1}$ relative to the band at 545 cm$^{-1}$). This is very likely due to an electronic process during the Raman measurements. The aerosols were measured on aluminium substrate that can enhance the electronic process during the Raman measurements. The aerosols ratio of few bands (especially for the band centred at 520 cm$^{-1}$) are comparable with the Raman spectrum of SrTiO$_3$ (sample S1).

Figure 11. Raman spectra comparison with sample SZ50. (a) Aerosols of sample SZ50, SYZ2 and S1. (b) Aerosols of sample SZ50, SYZ1 and Z1. [Colour figure can be viewed at wileyonlinelibrary.com]

Discussion

The elemental composition of the aerosols created by the experiments with strontium, yttrium and zirconium titanate deviated from the starting material for the aerosols with a smaller AED. These phenomena were already clearly visible for the aerosols of SrTiO$_3$, Y$_2$Ti$_2$O$_7$ and ZrTiO$_4$ separately. Strontium concentrates...
in the agglomerates of smaller particles, while yttrium and zirconium are less present in the smaller aerosols. In the samples where strontium and one or more of its daughter nuclides are present, the results show a combination of the behaviour of the individual materials. Because the difference between the elemental ratios and their theoretical value is not proportional to the age of the samples, age determination of the source material is not possible by analysing the ratio in the smaller aerosols produced by phase transition.

With a smaller AED, the experimental data reveal that titanium oxide is present in the aerosols of the samples with significant yttrium or zirconium content. In these particles, a lower percentage of yttrium and zirconium and a higher percentage of titanium are measured by EDX analysis, and also, the Raman spectra reveal titanium oxide. This is considered to be the main reason why the zirconium content in the aerosols of the samples that mimic older materials does not exceed the strontium content: a higher amount of yttrium and zirconium titinate in the material before the RDE results in a higher amount of titanium oxide in the aerosols. Whether this is also the case for the bigger individual particles cannot be determined because the individual particles are too small to perform Raman spectroscopy on.

Another consequence of the fact that titanium oxide was present in the aerosols is that the aerosols in RDD scenarios possess an additional health risk, besides the radiological risk. It is reported that titanium oxide nanoparticles in the rutile crystalline form can cause cytotoxic, neoplastic and genotoxic effects.[3]

The Raman spectra of the aerosols with strontium titanate also showed first-order Raman scattering. This is an interesting outcome because first-order Raman is symmetrically forbidden in single-crystal strontium titanate. It is therefore suggested that the aerosols contain impurities and have many grain boundaries that allow the first-order Raman scattering to dominate in the spectrum.

Conclusion

The ratio between parent and daughter nuclides is an important parameter in RDD scenarios, because this is used in nuclear forensics to determine the age of the material. We have used fast laser heating to produce aerosols of a material often found in RTGs, SrTiO₃. To investigate the behaviour of SrTiO₃, we have prepared pure and mixed samples mimicking the parent to daughter ratios. In earlier experiments, it was already shown by SEM analysis that two types of aerosols are created. The bigger individual aerosols show a ratio that stays close to the value that would be anticipated by the composition of the initial material used in the RDD and agglomerates of smaller aerosols in which the presence of the daughter nuclides reduces significantly. For these smaller aerosols, age determination of the original material can be ruled out; for the bigger aerosol, stronger experimental evidence with smaller standard deviations is needed to determine their usefulness for this purpose.

List of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AED</td>
<td>aerodynamic equivalent diameter</td>
</tr>
<tr>
<td>BSE</td>
<td>backscatter electron</td>
</tr>
<tr>
<td>TUD</td>
<td>Delft University of Technology</td>
</tr>
<tr>
<td>EC</td>
<td>European Commission</td>
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<tr>
<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
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GENTLE Graduate and Executive Nuclear Training and Lifelong Education

ITU Institute for Transuranium Elements

JRC Joint Research Centre

MOUDI Micro-Orifice Uniform Deposit Impactor

RADES radiological dispersion events setup

RDD radiological dispersal device

RDE radiological dispersion event

RTG radioisotope thermoelectric generator

SE secondary electron

SEM scanning electron microscopy

XRD X-ray diffraction

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References


Supporting information
Additional Supporting Information may be found online in the supporting information tab for this article.