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Other Technical Applications of Strontium Containing Materials

The properties and application fields of other strontium containing materials are shortly described in this chapter. Although these material and substances shouldn't be directly related to strontium aluminate cements or strontium aluminates, this survey may be illustrative for the importance and mutual relationships between individual strontium bearing materials.

1. Phosphors

Some amorphous calcium aluminates are photosensitive and thus are potential candidates for optical information storage devices [128,790,810-813], hence the research on the strontium aluminates is recently very intensive. Strontium based aluminate phosphors (Table 1) are well known for their high quantum efficiency, long-lived afterglow, good chemical stability, and other excellent luminescent features, which make them appropriate candidate to replace the traditional II–VI based phosphors. These materials are successfully used in various applications like luminous paints for highways, airports, buildings, ceramic products, textile industry, dial plates of glow watches, warning signs, escape routes, etc. [814]. The following properties are often mentioned with regard to these compounds:

- **Phosphorescence:** when the substances slowly re-emit absorbed electromagnetic radiation (usually UV) in the form of visible light. The same effect, but absorbed energy is re-emitted immediately, is termed as **fluorescence**.
- **Thermoluminescence:** is a process at which the substance releases high-energy radiation in the form of visible light upon heating, which enables electrons to return to their positions.
- Mechanoluminescence: is a process at which the mechanical action causes emitting of light.

In order to investigate their properties, various strontium aluminate phases occurring in the $SrO - Al_2O_3$ system were synthesized using the solid-state synthesis as well as nontraditional synthesis routes described in Chapter 9.

According to the **Blasse's theory** [827] on the energy transfer mechanism in oxide phosphors, the critical energy transfer distance (R_c) can be calculated from the concentration quenching data using the following equation:



$$R_c = 2\left(\frac{3V}{2\pi x_c N}\right)^{1/3} \tag{1}$$

Where x_c is the critical concentration, N is the number of host cations in the unit cell of volume V. The luminescence of $Sr_{3-n}Ca_nAl_2O_6$: Eu^{2+} phosphor that is completely solid solution of $Sr_3Al_2O_6$ and $Ca_3Al_2O_6$ can be shifted from 618 (orange) to 655 nm (red) with the increase of Ca/Sr ratio [378].

Phase	Dopant/ activator							
	Eu ²⁺ /Eu ³⁺	Dy³+	Sm³+	Ce ⁴⁺	Gd³+			
Sr ₄ Al ₂ O ₇	Red/orange [815, 816]	Blue and yellow [816]						
Sr ₃ Al ₂ O ₆	Red/ orange [814, 817-819]			Blue [820]				
SrAl ₂ O ₄	Green [821, 822]	Green [823, 824] ¹⁾	Orange [749] ²⁾	Green [763] ³⁾	Blue [821] ⁴⁾			
SrAl ₄ O ₇	[825] ⁵⁾							
SrAl ₆ O ₁₉	Violet [826] ⁶⁾							

¹⁾ Luminescence at 560 nm (green) and 595 (orange).

Table 1. Luminescence of some phases of SrO-Al₂O₃ system activated by commonly used ions.

REE activated strontium silicates, aluminosilicates, borates, zirconates (AZrO₃, A=Ca, Sr, Ba) and hafnates (SHO) such as strontium metasilicate (SrSiO₃:REE) [828-831], strontium orthosilicate (Sr₂SiO₄: REE) [832-838], glasses and glass-ceramics [839-847], SrZrO₃ [848-851] and SrHfO₃ [851-853] also show the photoluminescent properties.

2. Strontium containing bioactive cements

Although strontium is not considered as an essential element and does not have any known biological role, it is present in all living organisms. Strontium resembles the calcium element in its properties; like calcium, it is taken up and preferentially located in bones. Here, strontium can have both beneficial and deleterious effects in humans depending on the amount taken up [854]. Strontium ranelate ($C_{12}H_6N_2O_8SSr_2$), a pharmacologic agent used to treat individuals

 $^{^{2)}}$ Enhanced by B_2O_3 . Three main emission peaks at 562, 596 and 643 nm. The most intensive in orange.

³⁾ The second excitation peak in ultraviolet 381 nm.

⁴⁾ SrAl₂O₄:Eu²⁺, Gd³⁺phosphor.

⁵⁾ Green doped by Cu.

⁶⁾ Intensive emission at 397 nm and two weak bands at 594 and 615 nm (orange).

with osteoporosis, is indicated to be used in Europe and Australia but not in Canada or in the United States. Similar efficiency to delivery strontium to bones of animals was found for strontium citrate [855].

Injectable acrylic bone cements are widely used in orthopedic surgery to fix artificial prostheses. Conventional polymethyl methacrylate (PMMA) bone cement has been successfully used in arthroplasties of hip, knee and other joints for the fixation of polymer or metallic prosthetic implants to living bone; however, it still has some potential problems and risks, such as poor adhesion of bone cement to bone surface and high exothermic reaction during the polymerization [856, 857].

The size and morphology of individual particles, as well as the kind and extent of isomorphous substitutions greatly affect many physico-chemical properties of apatites. The great variety of possible cationic and anionic substitutions is justified by high stability and flexibility of the apatite structure. The unit cell of stoichiometric crystalline hydroxyapatite hosts 10 cations arranged in two non-equivalent positions: four at the M(1) site aligned in the column, each surrounded by nine oxygen atoms, and six at the M(2) site arranged at the apexes of "staggered" equilateral triangles, each surrounded by seven oxygen atoms. Among the bivalent cations which can replace calcium in Ca-HA, strontium has attracted a remarkable interest for its possible biological role [858-860].

Apatites are a family of inorganic crystalline compounds of general formula M₁₀(XO₄)₆Y₂, where M is usually a bivalent cations, such as Ca²⁺, Sr²⁺, Ba²⁺, Cd²⁺, Pb²⁺, but monovalent and trivalent cations, such as Na⁺, K⁺ and Al³⁺, can be hosted as well. XO₄ is usually PO₄³⁻, VO₄³⁻ or AsO₄³⁻, but possible substitutions also include SiO₄⁴⁻, CO₃²⁻, and SO₄²⁻. Y denotes monovalent anions¹ OH⁻, F⁻, Cl⁻ or Br⁻ [860, 861].

Strontium stimulates the bone formation and has been recently used to treat osteoporotic spinal fractures and other related osteoporosis [862,863]. The bioactive bone cements based on strontium hydroxyapatite ((Sr, Ca)₅(PO₄)₃(F, OH), Sr-HA or Sr-HAP, space group P 6₃/m) powder and Bis-GMA based resin were extensively studied as promising biomaterials [864-868]. The precipitation techniques [859] or hydrothermal syntheses [869-871] are usualy applied for the preparation of Sr-HA. The hydroxyapatite cements are considered as stronger than brushite cements [872] discussed below.

Calcium phosphate cements (CPC) are suitable materials for local delivery systems in osseous tissue since they can simultaneously promote the bone regeneration and prevent it from infectious diseases by releasing the therapeutic agents. Recent advances in CPC technology result in the enhancement of manipulation, applications and osteoconductive properties of these cements. These improvements allow the CPCs to be tested as carriers for local delivery of drugs and biologically active substances such as growth factors. Low-temperature setting of CPCs allows the incorporation of heat-labile medicaments and substances into the cement matrix during its preparation. Secondary CPCs which set (Eq.2, [881]) by the entanglement of brushite crystals (CaHPO₄·2H₂O) draw the attention as drug-delivery systems mainly due to

¹ Fluoroapatites obtained by the simultaneous substitution of Ca and PO₄³⁻ by REE and SiO₄⁴⁻ are described in Chapter

their biodegradability. Ionic substitution in ceramic biomaterials is a reliable approach to alter the properties like crystallinity, solubility and biological performance. The Sr-substituted calcium phosphate cement releases Sr^{2+} ions at the dose of 12–30 ppm with a zero-order kinetics [873-875].

$$Ca_3(PO_4)_2 + Ca(H_2PO_4)_2 + 8H_2O \rightarrow 4CaHPO_4 \times 2H_2O$$
 (2)

Brushite is formed on the calcite surfaces in caves in nature, where ammonium hydrogen phosphate or other related chemical in bat guano is the source of phosphate ions [876]:

$$(NH_4)_2 HPO_4 + Ca^{2+} + 2 H_2O \rightarrow CaHPO_4 \times 2H_2O + 2 NH_4^+$$
 (3)

It is supposed, that brushite act as the precursor at the formation of human bones and teeth [877]. Brushite is also used as food additive and a component of tooth paste. It can be synthesized in high purity by slow mixing of calcium chloride and disodium hydrogen phosphate [878].

However, brushite is metastable under physiological conditions [879] and the in vivo studies have shown that the brushite cement is highly resorbable [875]. The brushite crystal growth inhibition results in smaller-sized crystals, allowing them to pack closely together and improving brushite cement's mechanical properties. Furthermore, increasing of brushite cement density improves the cement mechanical properties by reducing the cement porosity that is inversely proportional to the cement strength. This can be achieved by increasing the conversion of β -TCP (calcium triphosphate, $Ca_3(PO_4)_2$) to brushite [872,874,879-881]. Although TCP exhibits the bioactivity [882] its instability above the pH of 4.2 generally leads to the interaction with water on its surfaces in body fluid [883,884]:

$$4 Ca3(PO4)2 + 2H2O \rightarrow Ca10(PO4)6(OH)2 + 2Ca2+ + 2 HPO42-$$
(4)

Brushite crystals show great variety of morphologies depending on the chemical conditions. Prismatic crystals precipitate from highly concentrated solutions, whereas tabular crystals are formed from more diluted solutions. Irregular crystals, limited by rounded edges or incomplete faces are common at all concentrations. The formation of twins according to [010] is also common [876].

Anhydrous form of brushite (monetite, CaHPO₄), is also useful biomaterial for the bone regeneration. Monetite can be prepared via two ways [876,885]:

1. Thermal dehydration of already set brushite cements that can be expressed by equations:

$$CaHPO_4 \times 2H_2O \xrightarrow{110-215^{\circ}C} CaHPO_4 + 2H_2O$$
 (5)

$$2 \operatorname{CaHPO}_{4} \xrightarrow{450^{\circ} C} \operatorname{Ca}_{2}(P_{2}O_{7}) + H_{2}O \tag{6}$$

Modifying the precipitation conditions of brushite cements.

Strontium ions can be successfully incorporated into brushite crystals, but they have a negative effect on brushite cement cohesion. Both strontium and pyrophosphate ions have a synergetic retardant effect on the brushite cement setting reaction. As the ionic radius of strontium is higher than that of calcium, the brushite lattice parameters increase with the increase of strontium content [828].

3. Britholites

Britholites are phosphosilicate apatites, formed by the simultaneous substitutions of rare earth elements (REE=Ln³⁺, La³⁺, Nd³⁺, etc.) and SiO₄⁴⁻for Ca²⁺ and PO₃⁴. Britholites are considered to be particularly promising to be used as the matrices for the confinement of nuclear waste or for the preparation of luminescent pigments. Several processes were developed for the preparation of britholites. Usually, they are obtained via the solid state reaction at high temperature [886-889]. As the mechanochemical synthesis leads to the carbonated britholites, the heat treatment up to 1100 °C is needed for the preparation of pure britholites [890,891].

The synthesis of strontium fluorobritholites can be described by the following equation [890]:

$$SrF_2 + 3 SrCO_3 + (6 - x) / 2 Sr_2 P_2 O_7 + x / 2 La_2 O_3 + x SiO_2$$

$$\rightarrow Sr_{10-x} La_x (PO_4)_{6-x} (SiO_4)_x F_2 + 3 CO_2$$
(7)

4. Ceramics and fiber-reinforced Sr-celsian matrix composites

Barium feldspar (BaAl₂Si₂O₈, celsian, BAS₂) and strontium feldspar (SrAl₂Si₂O₈, Sr-celsian, strontian, strontium anorthite, SrAS₂) exhibit a very similar polymorphism. For this reason, the terms monocelsian (celsian) and hexacelsian are also often used in literature to denote the monoclinic and hexagonal species of SrAl₂Si₂O₈ and BaAl₂Si₂O₈, respectively. Paracelsian is another known monoclinic polymorph of celsian [893,892].

Celsian and Sr-celsian (Fig.1) are the materials of great technological interest due to their excellent thermal and electrical properties. The monocelsian form exhibits high melting point (1650°C) and low coefficient of thermal expansion (2.5 \cdot 10⁻⁶ K⁻¹). The hexacelsian form, the hightemperature metastable phase of strontium aluminosilicate, shows high coefficient of thermal expansion (8·10-6 K-1) and reversible phase transformations within 600-800 °C causing the volume expansion of approximately 3% [893-895,1012].

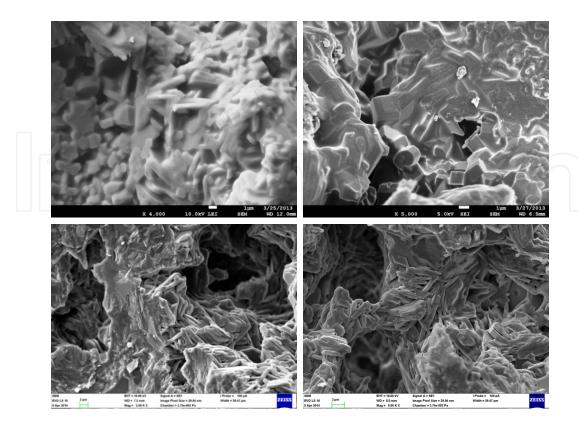


Figure 1. Synthetic anorthite [1011] and strontian prepared by the thermal treatment to 1300 and 1400 °C, respectively.

The properties of all three important feldspars, namely anorthite, strontian and celsian, are listed in Table 2.

Foldesman	Formula, space g. ¹⁾	Composition [% wt.] ²⁾			Density	Temperature [°C]	
Feldsapar		MeO	Al ₂ O ₃	SiO ₂	[g·cm ⁻³]	T _{M→H} ³⁾	Melting
Anorthite	CaAl ₂ Si ₂ O ₈ (<i>P</i> 1, <i>I</i> 11)	20.2	36.6	43.2	2.77	4)	~1550
Strontian	SrAl ₂ Si ₂ O ₈ (I2/c)	31.8	31.3	36.9	3.08	758	~1650
Celsian	BaAl ₂ Si ₂ O ₈ (I2/c)	40.8	27.2	32.0	3.39	1590/ 1650	~1760

¹⁾ Space group of monoclinic phase.

Table 2. Properties of MeAl₂SiO₈ feldspars.

 $^{^{\}rm 2)}$ Calculated according to the feldspar stoichiometry.

³⁾ Transformation temperature of monocelsian to hexacelsian.

⁴⁾ Triclinic anorthite has metastable hexagonal and orthorhombic polymorphs [1013].

In strontium aluminosilicate the hexacelsian phase may also exist as metastable. The existence of ferroelastic phase transformation to monocelsian at about 573 K followed by large expansion and the formation of microcraks is the main disadvantage for the application of hexacelsian. The kinetics and mechanism of transformation from hexacelsian to monocelsian, with and without doping with mineralizers, were reported, as well as the effects of mineralizers such as Li_2O , LiF, MoO_3 and TiO_2 .

The addition of SrO can enhance the transformation of hexacelsian to celsian. Moreover, the addition of SrO can effectively reduce the thermal expansion coefficient of the (Ba, Sr)O– Al_2O_3 – $2SiO_2$ ceramics [895,896,1022]. The processing and the properties of fiber-or whisker-reinforced celsian matrix composites were reported in the following papers [897-899].

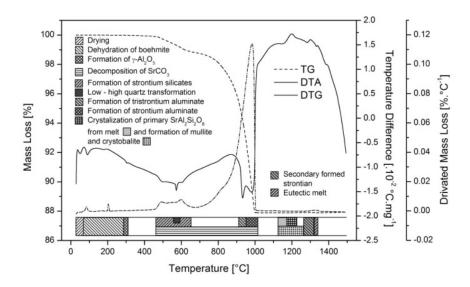


Figure 2. Thermal analysis of formation of strontian, the assessment using the heating rate of 10 °C min⁻¹.

Fig.2 shows the results of thermal analysis of mixture of strontium carbonate (SrCO₃), reactive alumina (the mixture of boehmite and X-Al₂O₃) and quartz (low quartz) in the ratio corresponding to the stoichiometric composition of strontian. Drying as well as the dehydration of boehmite and the formation of γ -Al₂O₃ take place up to the temperature of 450°C. Partial thermal decomposition of strontium carbonate within the temperature interval from 450 to 650 °C is associated with the formation of strontium silicates. The formation of strontium aluminates within the temperature range from 900 to 1020°C shows the same features as for SrAC raw meal (please see Fig.23 in Chapter 4).

The results indicate that strontian can be formed as primary and secondary strontian. Primary strontian crystalizes from non-equilibrium melt at the temperature of $1200 \,^{\circ}\text{C}$ and the process is accompanied by the formation of mullite $(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$ and the transformation of high quartz to cristobalite (c-SiO₂). The establishment of the equilibrium composition with increasing temperature leads to the formation of secondary strontian via the solid-state synthesis, where the reaction between mullite, silicate phases and strontium aluminate takes place. At the temperature of 1384 $^{\circ}\text{C}$, the eutectic melt appears.

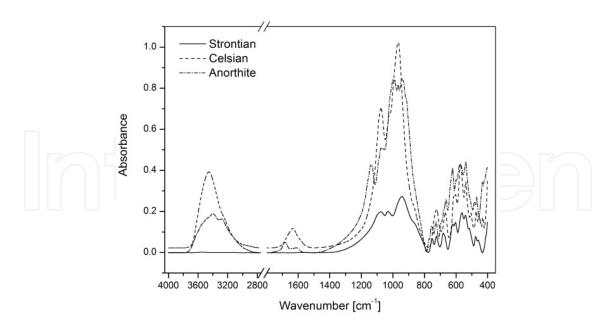


Figure 3. Infrared spectrum of strontian, celsian and anorthite.

Fig.3 shows the infrared spectrum of strontian after the thermal treatment, which is compared to the spectrums of celsian and anorthite. The spectrums of all samples show similar features with three main groups of bands [1025-1029]:

- 1. The spectral region from 1400 to 800 cm⁻¹ is related to the symmetric and antisymmetric stretching of Si-O-Si and Si-O-Al bonds in SiO₄ and AlO₄ tetrahedra.
- **2.** The spectral region from 800 to 650 cm⁻¹ shows the features of harmonic vibration of Si-Si(Al) bonds in corner sharing tetrahedra.
- **3.** The spectral region from 650 to 400 cm⁻¹ is related to the vibrations of tetrahedral ring, O-Si(Al)-O bending and coupling between the deformation and stretching modes.

All feldspars are tectosilicates and share similar "mirrored crankshaft-chain" frameworks of polymerized Al/Si tetrahedra. Therefore, the number and intensity of bands in the spectrum of feldspars increase with increasing degree of Al/Si ordering [1028]. The lattice modes and the bands related to M-O motions are located in the FAR infrared region [1029].

5. Glasses and glass ceramics based of strontian

The glass-ceramic materials, which are employed in the applications where good wear and erosion resistance are required, often at high temperature and in chemically hostile environments, are of increasing interest. Their optical properties are described in Chapter 10.1. For these reasons the knowledge of their chemical composition and mechanical properties is important, in order to determine in particular how various materials respond to the surface contacts. This kind of materials can be made either by traditional glass-forming technique, followed by the nucleation/crystallization heat treatment, or by the sintering of glass powders,

followed by the crystallization at higher temperatures. The latter technique is used especially where unusual product shapes are required, which cannot be obtained by common ways of glass shaping. Powdered glass, with the grain size less than 40-70 µm, with suitable binder is formed by pressing, casting in plaster molds or extruding [900-902].

Homogeneous and transparent glasses can be prepared within the SrAl₂Si₂O₈ (strontian)-Sr₂Al₂SiO₇ (helenite)-SrSiO₃ (strontium metasilicate) region of SrO-Al₂O₃-SiO₂ system [1014]. The thermodynamic model derived for the binary SrO – SiO₂ melts by R.-Serrano at al. [1023] is based on the consideration of the depolymerization reaction of SiO₂:

$$M^{2+}O^{2-} + \equiv Si - O - Si \equiv \rightarrow \equiv Si - O \quad (M^{2+}) \quad O - Si \equiv$$
(8)

or

$$O^{2-} + O^0 \to 2 O^-$$
 (9)

where M=Ca, Mg, Sr and Ba, O²⁻ is free oxygen ion, O⁰ is bridging oxygen bonded to two silicon atoms and O is oxygen bonded to one silicon atom.

Glass-ceramics based on strontian can be applied in aircraft industry for the preparation of radio-technical devices protected by radio-transparent barriers with the resistance to high temperatures due to their temperature stability, low thermal expansion coefficient, reduced electrical conductivity and dielectric losses. The selective growth of aluminium titanate (Al₂TiO₅, tialite²) and monoclinic SrAl₂Si₂O₈ is enabled by keeping the ratio of SrO: Al₂O₃ lower than one. That prevents the SrO-TiO₂-Al₂O₃-SiO₂ system from the crystallization of rutile and hexagonal polymorph of SrAl₂Si₂O₈ [1030].

SrO-Al₂O₃-La₂O₃-SiO₂-B₂O₃, La₂O₃-Al₂O₃-B₂O₃-SiO₂ and other strontium bearing glasses are concluded promising sealing materials for SOFC (Solid Oxide Fuel Cell) applications [1033-1035]. The preparation and the properties of mica glass-ceramics in the system $SrO\cdot 4MgO\cdot xAl_2O_3\cdot 6SiO_2\cdot 2MgF_2$ (x=1, 1.5 and 2) were described by Mllik at al. [1036]. The investigation of the crystallization and properties of the non-ferroelectric piezoelectric glass ceramics in the PbO-SrO-TiO₂-SiO₂ system demonstrates that the crystallization temperature of glass decreases with increasing mole fraction of PbO [1037].

6. Strontium containing bioactive glasses and glass ceramics

Bioactive glasses and glass-ceramics are widely studied due to their particular property of direct bonding to human bones through the formation of biologically active apatite layer at the bone/implant interface [903].

² Tialite ceramics and composites are intensively studied in the field of engineering ceramics for their low thermal expansion coefficient and high thermal shock resistance. Tialite is usually prepared from its constituting oxides mixed in the equimolar ratio and treated to the temperatures above 1300 °C. The product is used as a precursor for further fabrication process (shaping and sintering) [1031,1032].

The substitution of calcium by strontium results in a small but significant expansion of the glass network, which is associated with larger size of Sr²⁺ cation compared to Ca²⁺. The expansion of the glass network results in the weakening of the glass network and in associated decrease in the glass transition temperature and dilatometric softening point and in the increase in the thermal expansion coefficients [904]. The expansion of the network structure of glass increases the ion dissolution rates and has significantly pronounced effect on bone cells in vitro and in vivo. Therefore, bioactive response should be greater due to higher dissolution rate and biological effect of Sr on bone-forming cells. The slight supersaturation of physiological fluids with respect to Sr, Ca and phosphate causes the hydroxyapatite layer to occur more quickly [905]:

$$5 \operatorname{Sr}^{2+} + 5 \operatorname{Ca}^{2+} + 6 \operatorname{PO}_{4}^{3-} + 2 \operatorname{OH}^{2-} \longleftrightarrow \operatorname{Sr}_{5} \operatorname{Ca}_{5} (\operatorname{PO}_{4})_{6} (\operatorname{OH})_{2}$$
 (10)

The behaviour during the crystallization of glass–ceramic materials based on Na_2O –CaO– P_2O_5 – SiO_2 glass system modified by SrO/CaO and K_2O/Na_2O shows that potassium ions could be accommodated in the wollastonite structure while strontium ions might be incorporated in the sodium calcium silicate phase. The bioactivity studies on the prepared glass–ceramics samples show that the materials are capable of bonding with human bone due to the formation of apatite layer after the immersion in SBF solution. K_2O reduces the formation of apatite layer in the comparison with the potassium-free variety [903].

7. Strontium containing phosphorescent glasses and glass-ceramics

Glasses embedded with rare-earth (RE) ions are very attractive materials for the development of many optoelectronic devices, e.g. in fiber amplifiers, lasers, fluorescent devices and white light emitting diodes (LED) [843,906,907].

Long lasting phosphorescence (LLP) due to Eu²⁺ and Ce³⁺ ions was observed in Eu²⁺, Ce³⁺ codoped strontium borate glasses. The phosphorescence of Eu²⁺ decreases with the addition of Ce³⁺ because of the competition to obtain the trapped electron, and the phosphorescence of Ce³⁺ in the sample decays more quickly than that of Eu²⁺, which is suggested as the reason for the emission energy of Ce³⁺ to be higher or the distance between Ce³⁺ and electron traps of the glasses to be longer [908].

8. Strontium metal-organic framework

The research in the field of metal–organic frameworks (MOFs) has grown exponentially in the last decade because of the numerous potential applications such as in gas adsorption and storage, drug delivery, catalysis, fabrication of molecular sieve membranes and luminescent properties [909-911].

The strontium metal-organic framework of [Sr₂(BTEC)(H₂O)₄]•2H₂O was synthetized by Lo et al [911]. Sr²⁺ ion was nine-coordinated in the shape of a tricapped trigonal prism, SrO₉, and it bound six oxygen atoms from the carboxylate groups belonging to four BTEC ligands (H₄BTEC=benzene-1, 2, 4, 5-tetracarboxylic acid) and three oxygen atoms from the coordinated water.

9. Strontium titanate and other perovskites

Strontium titanates can be used as dielectric materials in high performance metal-insulatormetal (MIM) capacitors for analogue applications. The grain boundary barrier layer capacitors [912,913], oxygen gas sensors [914,915], substrates [916,917], catalysts [918] and solid oxide fuel cells (SOFC) anodes [919,920] are some of the most typical applications of these materials. Strontium titanate is also one of promising candidates for host materials in low-voltage electron-excitation displays because of its chemical and compositional stability and its optical band gap (3.3 eV).

Four phases of SrTiO₃ (ST, cubic perovskite with space group Pm3m), Sr₄Ti₃O₁₀ (tetragonal structure with space group I4/mmm), Sr₃Ti₂O₇ (tetragonal, double perovskite structure with space group I4/mmm) and Sr₂TiO₄ (quasi-two-dimensional K₂NiF₄ structure of Ruddlesden-Popper type, space group I4/mmm) were described in binary system of SrO – TiO₂. These phases can be prepared from the mixtures of SrCO₃ and TiO₂ in the ratio corresponding to the stoichiometry of required phase [921]. For the formation of those four compounds from their component oxides TiO₂ with rutile structure and SrO, the standard Gibbs free energy changes are given by [922]:

$$\Delta G_{(ox)}^{0}(SrTiO_{3}) \pm 89 / (J \cdot mol^{-1}) = -121878 + 3.881 (T / K)$$
(11)

$$\Delta G_{(ox)}^{0}(\mathrm{Sr_{4}Ti_{3}O_{10}}) \pm 284 / (J \cdot mol^{-1}) = -409197 + 14.749 (T / K)$$
(12)

$$\Delta G_{(ox)}^{\ o}(\mathrm{Sr_3Ti_2O_7}) \pm 190 / (J \cdot mol^{-1}) = -285827 + 10.022 (T / K)$$
(13)

$$\Delta G_{(ox)}^{0}(\operatorname{Sr}_{2}\operatorname{TiO}_{4}) \pm 110 / (J \cdot mol^{-1}) = -159835 + 3.770 (T / K)$$
(14)

Among the solid-state syntheses mentioned above, using the convectional [912,921,922] or the microwave sintering [923], the preparation of strontium titanate or its solid solutions via the sol gel method [918,924,925,926], the coprecipitation [926], the Pechini [920,927,928] or modified Pechini method [929], the solvothermal synthesis [926], the spray pyrolysis [930], and the solid mechanosynthesis [914,915,931] were reported. The mechanosynthesis of strontium aluminate is feasible only under highly energetic milling and failed for less energetic milling due to the thermodynamic restriction of the process [931].

Titanate-based perovskite-type oxides can be described by the general formula of MTiO₃, where M=Pb, Ba, Sr, Cd, Fe, Zn. Strontium titanate is paraelectric at room temperature and does not show the transition to ferroelectric phase when cooled to liquid helium temperature while barium titanate is ferroelectric at room temperature and shows the transition temperature of 120 °C. Depending on the Ba/Sr ratio, the properties of the solid solution (transition temperature, optical and electrical properties) of barium titanate and strontium titanate (Ba_xSr_{1-x}TiO₃, BST) differ over a broad range [924,932,933]. The addition of B₂O₃ to BST powder leads to the decrease of sintering temperature from 1350 to 900 °C. The temperature of maximum permittivity and the Curie temperature are not affected [934]. Plumbic titanate (PT) has high dielectric constant, but it is unsuitable for the applications mentioned above due to higher (490 °C) transition temperature (from ferroelectric tetragonal to paraelectric cubic phase). Depending on increasing Pb/Sr ratio in the solid solution (Pb_xSr_{1-x}TiO₃, PST), the Curie temperature decreases linearly with increasing content of Sr²⁺[935].

Due to their catalytic activity, ferroelectric properties, piezoelectric behaviour chemical and thermal stability and electrooptic propeties, perovskyte-type oxides (ABO₃) such as strontium niobate [936-938], cerate (SrCeO₃) [939-943], chromate (SrCrO₃) [944,945], molybdate (SrMoO₃) [944,946,947], SrMnO₃ [948,949], SrFeO₃ [950], SrCoO₃ [951,952], SrRuO₃ [948], etc. are intesively studied. These compounds belonging to the homologous series $A_nB_nO_{3n+2}$ are a special group of perovskite-related layered materials [938].

10. Strontium ferrites

Ferrite materials may be classified into three different classes; spinel ferrites, garnet ferrites and hexagonal ferrites. The magnetic spinel has the general formula of MFe_2O_4 , where M is the divalent metal ion, usually Ni, Co, Mn, or Zn. The garnet ferrites have general composition given by the formula $A_3B_3X_2O_{12}$, where A ions occupy distorted cube sites, while B and X are placed in octahedral and tetrahedral sites, respectively. In rare-earth iron garnets (REIG) $Ln_3Fe_5O_{12}$ and yttrium iron garnet $Y_3Fe_5O_{12}$ (YIG), Fe^{3+} ions show octahedral or tetrahedral environment, while rare-earth ions are in the centers of deformed cubes [953-955].

Hexagonal ferrites, MFe $_{12}O_{19}$ (M=Ba, Sr, Pb) with the magnetoplumbite structure have been important permanent magnet materials in microwave, small motor, and, more recently magnetic recording applications since their discovery in 1950s. It is well known that the coercive force of hexaferrites depends mainly on the crystallite size; high coercivity can be reached when the size of crystallites is ~ 100 nm. In order to improve the fundamental magnetic properties of hexaferrites, many studies have also been carried out concerning the cationic substitution. Some experiments used light rare-earth ions such as La (La $_x$ Sr $_{1-x}$ Fe $_{12}O_{19}$), Pr and other metal cations in the substitution for Sr (Ba) and Fe, respectively, taking into account the ionic radius of the elements [956,957].

Hexagonal ferrites, so-called hard ferrites, possess relatively high saturated and remnant magnetizations and exhibit high magnetocrystalline anisotropy. High heating effect can thus be expected. Iron ions occur at five different sites: the octahedral sites, crystallographically known as 2a, 12k, and 4f₂, and the tetrahedral sites 4f₁ and 2b. In the magnetically ordered state in BaFe₁₂O₁₉ or SrFe₁₂O₁₉, the 12k, 2a, and 2b sites have their spins aligned in parallel to each other and to the crystallographic c-axis, whereas those of 4f₂ and 4f₁ point the opposite directions [958].

Their structures of a polytypic nature can be conventionally often described in the terms of an intergrowth of the blocks S, R and T. The S block is a (111) slice of the common spinel structure, while R and T are the blocks of hexagonal symmetry which represent weak links in the magnetic exchange interactions. Among them let us mention the M phase as example, arising from the stacking of ... SRS*R*... type and the Y phase formed by stacking of ... $S_1T_1S_2T_2S_3T_3...$ type. Hexagonal ferrites are complex magnetic systems and offer several kinds of nonequivalent sites, octahedral, bipyramidal and tetrahedral, which can be occupied by diverse magnetic or non-magnetic cations. Their magnetic properties thus can be readily modified by changing the stacking of individual blocks and the composition in a desirable way [959].

Ferite materials can be prepared by various techniques including the solid-state synthesis [854,856,858], the sol-gel method [960,961], the coprecipitation method [962,963] and the combustion synthesis [964].

For the microwave applications, the dielectric properties such as dielectric constant and dielectric loss are very important as the dielectric constant affects the thickness of microwave absorbing layer and the dielectric loss factor ($tan \delta$) of a material determines the dissipation of electrical energy. This dissipation may be due to electrical conduction, dielectric relaxation, dielectric resonance and loss from non-linear processes. High performance devices require low dielectric loss because the lower it is the higher the efficiency and the lower the noise. The porosity of material also increases the dielectric loss and that may be due to the absorption of humidity by the pores of that material [963,965,966].

11. High-temperature ceramic superconductors

In 1986 Bednorz and Müller discovered the high temperature superconductivity by predicting that the JT (Jahn–Teller) distortion plays an important role in lanthanum copper oxides (LSCO) and thus the electron–lattice interactions are very strong in cuprates [967].

It was shown by the first-principle variational calculation of the spin-density-functional approximation, that when Sr²⁺ ions were substituted for La³⁺ ions in LSCO, the optimized distance between apical O and Cu in LSCO decreased with Sr concentration. As a result the elongated CuO₆ octahedrons by the JT interactions shrank by doping holes. This shrinking effect against the Jahn–Teller distortion is termed as "anti-Jahn–Teller effect" [968].

Strontium is used for the synthesis of ceramic superconductors for various systems. Some examples of these compounds are listed in Table 3. It should be noted, that all examples are ceramic conductors, but only the system with critical temperature (T_c) higher than 30 K can be considered as high-temperature superconductors. Although T_c is the most known parameter, there are two other parameters: B_c (critical magnetic field) and I_c (critical current density),

Superconducting system Superconductor (Abbreviation) T _c [K] Referen						
Bi–Sr–Ca–Cu–O (BSCCO)	Bi ₂ Sr ₂ CuO _{6+ δ} (Bi 2201)	< 20	[969, 970, 971]			
	Bi ₂ Sr ₂ CaCu ₂ O _{8+ δ} (Bi 2212)		85 (110) ¹⁾	[969-972]		
	Bi ₂ Sr ₂ Ca ₂ Cu ₃ O _{10+ δ} (Bi 2223)		110	[969-971, 973]		
Tl–Sr–Ca–Cr–Cu–O	TISr ₂ CuO ₅ (TI 1201)		70	[974]		
	(TI _{1-x} Cr _x)Sr ₂ CaCu ₂ O _{7-δ}	TI 1212	103	[974, 975]		
	$(TI_{0.5}Pb_{0.5})Sr_2Ca_2Cu_3O_9^{3)}$	TI 1223	130	[975, 976, 977]		
	Tl ₂ Sr ₂ CaCu ₂ O ₈₋	TI 2212	110	[974, 975, 978]		
	$(TI_{1-x}Hg_x)_2Sr_2CaCu_2O_{8-\delta}$		<45	[974, 975]		
		TI 2223	125	[975]		
Sr-doped La-Cu-O 2)	La _{2-x} Sr _x CuO _{4- δ}	LSCO	~12	[968, 979-981]		

¹⁾ In the Pb-doped systems ([Bi, Pb]:Sr:Ca:Cu).

Table 3. Examples of strontium bearing ceramic superconductors.

which both together provide the phase diagram for high temperature superconductors of the first and second type.

12. Heisenberg antiferromagnets

Two-dimensional triangular Heisenberg antiferromagnets (2DTHAF) have been the subject of intense research activity for a long time, both from the theoretical and experimental viewpoints [982,983].

From the experimental point of view, an important class of quasi-2DTHAF involves S=3/2 spins associated with Cr³⁺, in two families of layered chromites:

- a. Ordered rock-salt structures (ACrO₂ with A=Li, Na);
- **b.** So-called delafos-site compounds (MCrO₄ with M=Cu, Ag, Pd).

Recent works demonstrate that the α -ACr₂O₄ compounds (with A=Ca, Sr, Ba) should be included in the same class of materials.

 AM_2O_4 compounds usually crystallize in the $CaFe_2O_4$ type, but using high preparation temperature (higher than 2000°C), SrO reacts with Cr_2O_3 to form the compound with a new type of crystal structure. $SrCr_2O_4$ is a metastable substance stabilized by entropic effects, which crystallizes in the form of extremely thin two-dimensional sheets. The attempts to increase the

²⁾ High temperature superconducting cuprates (HTSC).

³⁾ The highest critical temperature in the system.

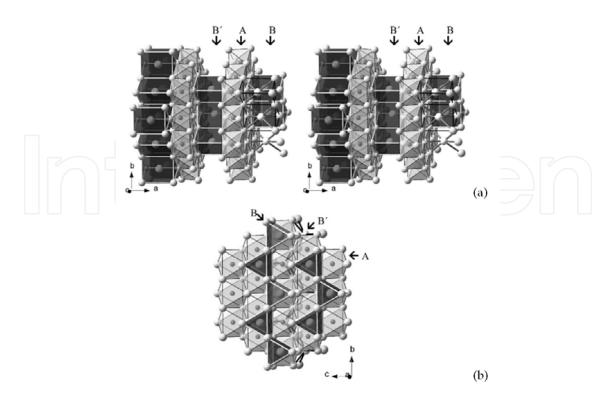


Figure 4. Crystal structure of SrCr₂O_a: (a) connection layers of CrO₆-octahedra (layer A), chains of SrO₆ trigonal prisms (layer B and B') and (b) connections of SrO₆ prism chains with CrO₆ octahedra of layer (A) using triangular polyhedral faces. The end of one SrO₆ prism chain is situated in layer (B') above both sides of layer (A) [984].

thickness of the crystals by annealing at lower temperatures (900-1000 °C) led to the distortion of the metastable crystal structure in all cases [984].

The SrCr₂O₄ type exhibits the layers (A) consisting of close-packed planes of CrO₆-octahedra. These layers (A) are connected by SrO₆ trigonal prisms (Fig.4(a), dark polyhedra, bright edges). SrO₆-prisms themselves form _∞[SrO₄]-chains crossing the crystal along [010]. The connections between [SrO₄]-chains and the CrO₆-octahedra are illustrated in Fig.4(b) [984].

13. Strontium carbide, nitride and silicide

Strontium carbide (SrC₂) was synthesized for the first time by Moissan [985-987] from Sr(OH)₂ or SrCO₃ with sugar coal in an electrical arc furnace at the end of 1800s. Binary carbides can be described by the general formula AC2, where A=Mg, Ca, Sr, Ba, Rb. At ambient conditions SrC₂ crystallizes in the tetragonal CaC₂(I) structure (I4/mmm). The C₂² dumbbells are aligned along the tetragonal c axis in these structures. At the temperature about 643 K a phase transition to a cubic high temperature modification occurs, which is analogous to Fm 3 m structure of CaC₂(IV) [988-990]. At low temperatures a partial transformation of SrC₂ (I) to monoclinic low-temperature modification (C2/c, SrC₂ (II)) was observed. This transformation starts at room temperature and levels out at about 80 K [989].

Strontium nitride (Sr_2N) crystallizes in a layered structure of the anti- $CdCl_2$ type. In Sr_2N , close-packed Sr atomic layers sandwich nitrogen atoms to form the Sr_2N layers, and the gaps between the layers are considerably expanded (the Sr–Sr distance across the gap reaches 0.473 nm, while that in the Sr_2N layer is 0.352 nm), indicating the van der Waals character of the gaps (Fig.5). Recently, the series of new compounds such as Sr_4N_3 , SrN, and SrN_2 have been reported as derivatives of Sr_2N [991, 992].

The metals from the second group (A) form nitrides with A–N bonding and the structures change dramatically with the descent in the group; the lighter metals (Be–Ca) form ionic, insulating or semiconducting, salt-like compounds whereas the heavier members of the (Ca–Ba) group form subnitrides with low-dimensional structures and metallic properties. The simple reaction chemistry of subnitrides is intriguing. Layered subnitrides A_2N (A=Ca, Sr, Ba) provide a structural basis for the inclusion of anions from simple spherical species such as halides (A_2NX , X=F, Cl, Br, I) to form more complex, anisotropic entities such as N_2^2 -and CN_2^2 -[993]. The optoelectronic applications, such as in the field of high performance light emitted diodes, are possible for strontium-germanium ternary nitrides (A_2MN_3 , where A=Sr, Ba and M=V, Ta, Nb) α -and β -Sr₂GeN₂ [994] and Sr₂TaN₃ [995].

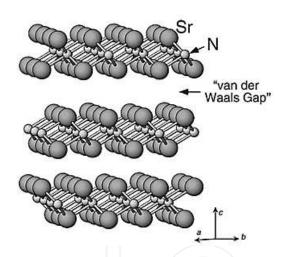


Figure 5. Crystal structure of Sr₂N [991].

In recent years an increasing attention has been drawn to the alkaline-earth metal (AEM, (Ca, Sr, Ba)Si₂) silicides, in particular with the ratios of 2:1, 1:1 and 1:2, due to their semiconducting and superconducting properties [996]. Pseudo-binary hexagonal **strontium silicides** SrNi_xSi₂. (0.1 < x < 0.7) were prepared by arc-melting. The phase shows the superconductivity with T_C of 2.6 K. Besides, for these silicides the non-conventional AlB₂-like phase may be stabilized by partial replacement of Si by sp metals (Al or Ga); in order to turn the lattice into pseudobinary silicides Sr(Al, Ge)_xSi_{2-x}. The superconducting transition at the temperature T_C of 5.1 K was found for this compound [997]. The ternary Sr-Al-Si system produced the clathrate type I structure by arc melting of the appropriate elemental combinations. The layers are interspersed with Si atoms. The AAl_{2-x}Si_x (Al=Ca, Sr; x=1) phases crystallize as the AlB₂-type structures (P6/mmm) [998,999].

The formation of ternary hydrides (MTrTtH, where M=Ca, Sr, Ba, Tr=Al, Ga, In and Tt=Si, Ge, Sn) was also reported. SrAlSiH crystallizes in the layered structure (P3m1), where Al and Si are in ordered hexagonal sheet with hydrogen surronding a Al on one side only [1000]. SrAlGeH can be synthetized by hydrogenating the intermetallic AlB₂-type precursors (SrAlGe) or by the reaction of SrH₂ with a mixture of Al and Ge in the presence of pressurized hydrogen [1001].

14. The effect of strontium on the properties of alloys

Magnesium (Mg) alloys are known for their remarkable strength-to-weight ratio (density 1.74 g cm⁻³) and are therefore being considered as excellent material candidates in aerospace and transportation industries, where the performance and fuel economy are of major importance. However, insufficient control of room temperature formability compared to currently used aluminum alloys for example, as well as plastic anisotropy has restricted the extended use of Mg alloys. In this context, several attempts have been made to introduce various alloying combinations, which linked with advanced processing techniques have the potential to minimize the formation of strong textures during hot deformation which are responsible for observed poor formability of Mg alloys. Relevant improvements of properties and corrosion resistance have been reported in the case of Rare Earth elements (REE) which, however, are relatively cost prohibitive [1038,1039].

Strontium and calcium are initially introduced to Mg alloys in order to replicate the effects of REE. Thermally resistant Sr-rich precipitates form the unique Mg-Al-Sr high temperature creep resistant alloys, which are successfully used in casting automotive engine blocks. Strontium was also used to develop wrought Mg alloys where thermally stable Sr-rich precipitates were the effective particle stimulated nucleation (PSN) sites during hot deformation and were capable of reducing the texture anisotropy by nucleating into randomly orientated grains. It was also noted that when the amount of Sr increased above certain values, such precipitates could also act as the crack nucleation sites and therefore reduce the ductility. Furthermore, the effect of Sr on the twinning of a Mg-Al alloy caused by the changes in solid solution composition was also investigated [1039-1040].

The effects of Sr in AZ31 are dependent on the concentration of Sr in the alloy and the type of second phase which precipitates. When added to AZ31, Sr forms Al-Sr, Mg-Al-Sr, Mg-Sr and Sr-Zn precipitates. In the Mg-Al-Zn system Sr prefers to bind to Al rather than to other elements. Because of this high affinity of Sr to Al, all the precipitates in the AZ + Sr system could be classified into two groups: precipitates with Al and precipitates without Al [1040].

The additions in the range of a few 100 ppm of Sr, Na, Ca, Ba or Eu modify the eutectic Si morphology of Al-Si alloys from coarse plate-like into fine fibrous and have a beneficial effect on both strength and ductility [1041]. Strontium decreases the volume percent, size and number of settled intermetallic compounds in A380 aluminium alloy. The distribution of alloying elements in Sr-modified melt is also more homogenous than in unmodified melt [1042].

15. Immobilization of strontium radionuclides

Strontium radioactive isotopes Sr-89 and Sr-90 emit high-energy beta radiation. They are extremely hazardous because they deposit in bones replacing calcium. Their radiation can damage bone marrow and blood-forming organs, inducing cancer [91]. The radionuclide solubility is one of the factors, along with the sorption and inventory, which can determine the 'source term' for potential migration to the far away field of a nuclear waste repository. Several processes can affect the concentration of radionuclide in water in pores of cement [1002,1003]:

- 1. Precipitation as the simple salt
- 2. Coprecipitation with other phases;
- 3. Incorporation in lattice of major cement hydration products (solid solution);
- 4. Sorption at hydrous surfaces (chemisorption, adsorption);
- 5. Complex and colloid formation in aqueous phase.

The absorption is the incorporation of a sorbate within a physical or molecular structure of a sorbent, i.e. the sorbate has the access to the bulk, not just to the surface, of sorbent. Physical adsorption can be divided into three types:

- 1. Surface complexation, which is a mixture of chemical and electrostatic interactions;
- **2.** Ion exchange, which is an example of electrostatic adsorption due to columbic forces of attraction between charged sorbate species and the sorbent;
- 3. Other mechanisms, e.g. solid-solution formation, coprecipitation.

The binder most commonly used for the immobilization of toxic and radioactive waste is Portland cement. The most important reactions of cement with waste are those which lead to binding, i.e. chemical reaction and formation of thermodynamically stable or near stable product. The behaviour of Sr in cements might be expected to mirror that of Ca. However, it is soluble in NaOH or KOH to such extent that Sr(OH)₂ precipitation in cements is unlikely [12, 1002, 1004].

The major amount of Sr was incorporated into the calcium aluminium sulphate hydrates. Appreciable substitution of strontium in Aft and C₃AH₆ was demonstrated, and was thought by the authors to be likely in AFm-type phases. The structure of AFt has a range of structural sites which can be occupied by both, cations and anions. Therefore, cements high in Ca and Al, such as high alumina cements (HAC) or the mixtures of alumina cement with Portland cement, will have the best 'sorption' characteristics for Sr. The leaching experiments on Sr dopped pastes, in conjunction with the consideration of the effect of carbonation, indicated the coprecipitation of SrCO₃ to be a solubility-limiting process for the release. An ettringite analogue³ with Sr replacing Ca was reported [12,1002,1004]. On the other hand, delayed formation of ettringite leads to cracking of the test specimens. This process is associated with increasing leachable surface and decreasing physical stability [12].

Cement based materials were used in the radioactive waste management to produce stable waste forms and to build engineering barriers in disposal facilities. The immobilization of low and intermediate level radioactive wastes in cementitious matrices is the most commonly used technique to produce inexpensive waste matrix that complies with the regulatory requirements. Immobilized waste forms can be safely isolated from the biosphere for a long time in a radioactivewaste repository. Conventional cementitious waste matrices consist of waste, cement, additives and water. The additives (blast furnace slag, fly ash, kaolin, zeolites and bentonite) are used to enhance the mechanical performance of the waste matrix and/or to reduce the leachability of problematic radionuclides e.g. ¹³⁷Cs, ⁶⁰Co, and ⁹⁰Sr [1005-1007].

The binding of radionuclides by a cement matrix is determined by their chemical nature and is not affected by their radiation characteristics. In most nuclear wastes the present radionuclides constitute only a small fraction of the total mass, and are intermixed with non-radioactive species. If some of them possess chemical toxicity, such products are classified as mixed wastes. The immobilization of heavy metals (As, Ba, Cd, Cr, Hg, Pb, Zn...) is generally attributed to the precipitation of insoluble hydroxides in the high pH environment [12].

Blended cement⁴ with bentonite was proposed as a buffer and/or shaft seal in geological disposal for nuclear wastes due to its low permeability, chemical and physical stability, and compatibility with different host environments. The utilization of bentonite as liner and waste matrix additive was supported by the availability of smectite ion exchange and amphoteric surface complexation sites for the adsorption of radionuclides [1005, 1008]. The blends of Portland cement with zeolite are also promising ion exchange materials for the removal of radioisotopes from aqueous nuclear wastes because of their selectivity, radiation and thermal stability, and good compatibility with the cement matrix [1006].

The presence of blast furnace slag in Portland cement reduces the leachability of technetium and chromium. The addition of fly ash or silica fume into the cementitious system reduces the leachability of heavy metals, mainly by reducing the content of free calcium hydroxide in hardened paste [12].

16. The biological role of strontium

Natural strontium is a mixture of four stable isotopes: 84Sr (0.56%), 86Sr (9.86%), 87Sr (7.02%), and 88Sr (82.56%). Strontium comprises 0.02-0.03% of the earth's crust from where strontium dissolved in water derives. Its concentration in soil and drinking water varies between 0.001 and 39 mg dm⁻³. Normal daily intake contains 2-4 mg Sr per day, most of it is derived from vegetables and cereals. Thus, the amount of Sr in food of Western countries is negligible compared to Ca. The intake of Sr depends on the Sr contents in nutrients, and for plants the concentration of Sr correlates with the Sr content in soil, which is much lower than that of Ca [1015].

³ Structure of ettringite and ettringite analogue are described in Chapter 8.2.

⁴ Blended cements were defined in the introduction of Chapter 7.

Sr has never been shown to be an essential element, that is, causing death when absent, but Sr may promote growth in some plants. Since strontium given as strontium ranelate (please see Chapter 10.2) augments bone Ca in experimental animals and reduces the fracture rate in osteoporotic patients, it could be hypothesized that one feature of osteoporosis may be a certain degree of Sr deficiency, but the data on normal content of Sr in bone are scarce. One investigation of trace elements in iliac crest biopsies of an experimental osteoporotic rabbit model did not show reduced bone Sr levels. However, it was shown that among the trace metals present in human bone, Sr was the only one that was correlated with bone compression strength [855,1015,1016].

The toxic symptoms in human due to overdosing on Sr have not been reported. However, the intravenous administration of high doses of Sr induces hypocalcaemia due to increased renal excretion of Ca. The only stable Sr-containing chemical that is considered to be harmful to humans in small amounts is strontium chromate, the toxicity being caused by the chromium which is a genotoxic carcinogen [854,1015,1017].

Strontium in human biology and pathology has attracted less attention than the other two important divalent metals calcium and magnesium, and over the years it has been an object of academic rather than clinical interest. Although this is still true, that there is an increasing awareness of the biological role of Sr after the development of the strontium ranelate drug, which has recently been shown to reduce the incidence of fractures in osteoporotic patients. Radioactive Sr isotopes are dealt with only when they are used for physiological or diagnostic purposes [1015,1018]. Strontium isotope ratio analysis also becomes common in archaeological investigations [1019-1021].