

Glass Crystalline Materials

Subjects: [Energy & Fuels](#) | [Materials Science, Composites](#)

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Glass crystalline materials (GCM) are composite solids consisting of both vitreous and crystalline phases. The major component can be the crystalline phase with a vitreous phase acting as a binding agent or alternatively the vitreous phase can be the major component, with crystalline particles dispersed in the glass matrix.

high level radioactive waste (HLW)

radionuclide partitioning

immobilisation

melting

sintering

crystalline matrix

vitreous matrix

glass crystalline materials (GCM)

1. Introduction

GCM are of increasing interest as advanced nuclear wastefoms combining the advantages of vitreous and crystalline matrices. The GCM are versatile wastefoms envisaged for a wider use to immobilise various types of both radioactive and chemically hazardous wastes. They can be produced either via low temperature sintering using precursors composed of glass frit, oxides, and crystalline phases or through conventional melting aiming to produce first a parent glass, which is then crystallised by a controlled thermal schedule to obtain target crystalline phases within the GCM.

The spent nuclear fuel (SNF) reprocessing generates radioactive wastes, including high level radioactive waste (HLW), which is industrially immobilised in the Na-Al-P glass in Russia and A-B-Si glass elsewhere, where A stands for alkaline elements. By 2013, there were about 30,000 accumulated tonnes of vitrified HLW overall in the world ^{[1][2]}. Considering the processing rates of vitrification facilities ^{[2][3][4][5][6]}, the current mass of vitrified HLW can be estimated at about 35,000–36,000 tonnes, of which almost 80% are A-B-Si, and the rest are Na-Al-P glasses. Vitrification of HLW is, however, not the optimal method of immobilisation due to the relative low radionuclide loading of glasses and their susceptibility to crystallisation, which can begin immediately after the melt pouring into canisters due to the residual heat of the melt ^{[6][7]}. Partitioning of HLW radionuclides onto groups can provide a better solution for their immobilisation by incorporation within crystalline lattice of silicates, titanates, zirconates, and phosphates. Their natural analogues are minerals zircon, britholite, pyrochlore, zirconolite, murataite, perovskite, monazite, and garnet ^{[8][9][10][11][12][13][14][15][16]}. Fission products (Cs, Sr) can be isolated in both crystalline phases such as hollandite, pollucite, perovskite, langbeinite, and glasses. Glass crystalline materials (GCM) with the same mineral-like phases are optimal for wastes of complex composition. The major component of GCM may be either the crystalline phases with the glass acting as a binding agent or alternatively the vitreous phase may be the major component, with crystalline particles dispersed in the glass matrix ^{[17][18][19][20][21]}.

2. GCM with Mineral-Like Phases

2.1. Importance of Novel Matrices

Much attention is paid to the modernization of existing glass matrices, as well as the search for new types of wastefoms, for example, for HLW radionuclide fractions. Partitioning of HLW and incorporation of the most dangerous long-lived actinides and fission products in a compact and capacious matrix will improve the use of underground repository space. This will reduce the need for the construction of new storage facilities and lead to savings in finances and time for their search and construction. Potential novel matrices for HLW immobilisation are crystalline and GCM which have been studied since the 1970s, almost simultaneously with research of glasses [\[22\]](#) [\[23\]](#) [\[24\]](#) [\[25\]](#).

2.2. Crystalline Matrices

The best known crystalline wastefoms are the Synroc polyphase ceramic and the monophase NZP matrix. In the first, artificial phases of minerals with the structure of perovskite, zirconolite, pyrochlore, and hollandite serve as carriers of radionuclides and the HLW elements are distributed between them in accordance with the radius and charge of cations. The structure of the NZP matrix of the composition $\text{NaZr}_2(\text{PO}_4)_3$ as a natural analogue of the mineral kosnarite is formed by a three-dimensional network of PO_4^{3-} octahedra connected by vertices to ZrO_6 octahedra, and large Na^+ cations occupy voids. The HLW components can enter three positions of the structure: Alkalis, alkaline earths instead of sodium; REE and actinides are in the Zr position, hexavalent Mo replaces phosphorus, etc. Usually, there is an additional phase—REE phosphate with a monazite structure. Kosnarite, $\text{KZr}_2(\text{PO}_4)_3$ is a natural analogue of the NZP matrix, although unlike other phases (pyrochlore, zirconolite, brannerite, monazite, etc.), it does not contain radioactive elements such as U and Th [\[22\]](#). The waste loading of Synroc and NZP ceramics is about 20 wt.%. Crystalline phases for immobilization of waste have been overviewed in many publications such as [\[15\]](#) [\[16\]](#) [\[22\]](#) [\[26\]](#).

2.3. GCM as an Universal Nuclear Wasteform

GCM are thermodynamically more stable materials compared with homogeneous glasses. Indeed, the free Gibbs energy G_{GCM} of a GCM containing the volume fraction φ of crystalline phase will be:

$$G_{\text{GCM}} = \varphi G_{\text{C}} + (1 - \varphi) G_{\text{G}}$$

where the free Gibbs energy of crystalline phase G_{C} is lower than the free Gibbs energy of glass G_{G} . Thus, the driving force of crystallization of GCM toward a most stable fully crystalline material (for which $\varphi = 1$) will be smaller.

GCM containing both crystalline and glassy phases are optimal for radioactive waste of complex composition [\[8\]](#) [\[17\]](#) [\[19\]](#) [\[21\]](#) [\[22\]](#) [\[27\]](#) [\[28\]](#) [\[29\]](#) [\[30\]](#) [\[31\]](#) [\[32\]](#) [\[33\]](#) [\[34\]](#). Compared to homogeneous glassy materials, GCMs can incorporate larger amounts of waste elements and they can be produced using lower processing temperatures than those of

conventional melting. Indeed, hazardous and nuclear waste constituents can be immobilised both by direct chemical incorporation into the glass structure in a classical vitrification approach and by the physical encapsulation of the waste in a glass matrix, forming a GCM consisting of both vitreous and crystalline phases (Figure 1).

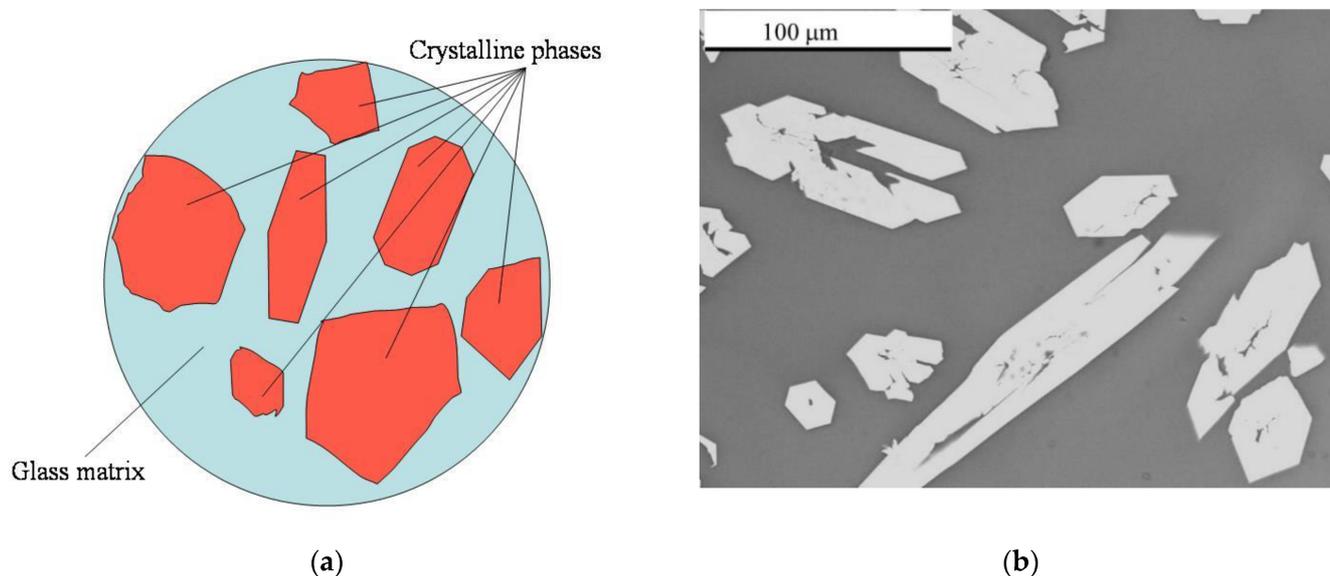


Figure 1. Schematic of a Glass crystalline material (GCM) nuclear wasteform (a) and SEM/BSE image (b) of a real specimen loaded with rare earth elements (REE)-imitator of actinides. Dark areas are composed of glass and light grains are crystals of britholite.

3. Conclusions

This entry focuses on GCM as versatile materials to immobilise nuclear waste^[35]. HLW derived in the close nuclear fuel cycle is currently immobilised into Na-Al-P and A-B-Si glasses using vitrification technology. Waste immobilisation in GCMs has emerged as a versatile technology enabling reliable immobilisation of complex and varying composition waste streams, including both radioactive and hazardous residues, which are otherwise difficult to immobilise using the traditional vitrification technology. The optimisation of the GCM phase assemblages as a function of waste stream composition is important for achieving simultaneously high nuclear waste loadings and corrosion resistance. Future research may focus on practical aspects of GCM utilisation through one or another technological process using either controlled devitrification of synthesized parent glasses or sintering routes using crystalline and vitreous precursors.

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