Mössbauer studies of materials used to immobilise industrial wastes

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Abstract The necessity to immobilise waste safely requires the development of stable materials. Mössbauer spectroscopy has been used to help understand and obtain desirable properties in alkali borosilicate glasses, phosphate glasses and vitrified sewage sludge ash. Phosphate glasses suitable for waste immobilisation have been microwaved and conventionally melted and differences reported. The environment of Fe in promising ceramics has also been studied. Mössbauer studies of irradiated vitrified wasteforms show their resistance to radiation damage.

Keywords Waste · Radioactive · Glass · Ceramic · Mössbauer · Industrial

1 Introduction

Modern society produces a wide range of toxic wastes. Some of the most potentially dangerous are nuclear wastes, with various levels of radioactivity. Other wastes, which present a significant hazard, include incinerator ash which contains harmful heavy metals. This means that safe immobilisation may be necessary to place the waste into a passively safe state, ready for disposal or, in some cases, re-use (although this is not an option for most radioactive wastes). Vitrification is the global method of immobilising high level liquid waste (HLLW) arising from nuclear fuel reprocessing and it is also an advantageous method of treating non-nuclear hazardous wastes such as sludges and ashes [1].

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Glass and ceramic host materials, to safely immobilise such wastes, require a combination of structural longevity and stability, compositional flexibility, thermal stability and chemical durability. Optimum properties are obtained by modifying the composition and production parameters. One component common to many radioactive and toxic wastes is iron, present at abundances [1] depending on the waste and the nature of the host. Iron substantially affects material behaviour and performance. ^{57}Fe Mössbauer spectroscopy has been used at the Materials and Engineering Research Institute (MERI) at Sheffield Hallam University to identify the valence state and local coordination environments of Fe in glasses and ceramics developed for waste immobilisation. This contributes to developing an understanding of the key composition / structure / property relations. For each group of our materials the focus of the work will be presented, with the key Mössbauer results, and conclusions at this stage.

2 Experimental

For all materials reported in this paper, room temperature Mössbauer spectra were collected relative to α-Fe using a constant acceleration spectrometer with a 25 mCi ^{57}Co/Rh source. Spectra were analysed using "Recoil" software [2].

2.1 Alkali borosilicate glasses

Alkali borosilicate glasses are globally the host material of choice to immobilise HLW (high level nuclear waste) [1, 3]. Glass "MW", originally designed to vitrify Magnox waste, has been successfully used to vitrify mixtures of Magnox and Thermal Oxide Reprocessing ("oxide") HLLW wastes since 1991 [1, 3]. Different levels of Fe_2O_3 are present in Magnox and Oxide wastes. We investigated the effects of Fe_2O_3 additions to MW glass on chemical durability, processing parameters and waste loading capacity [3]. Spectra were fitted with Lorentzian doublets and centre shift (CS) and quadrupole splitting (QS) parameters indicated that all Fe was present as $^{[4]}Fe^{3+}$ in all samples, thus increasing the connectivity of the glass network [3] and consistent with an observed durability increase.

2.2 Phosphate glasses

We have studied several phosphate glass types under consideration for the immobilisation of problematic wastes. Phosphate glasses may offer a number of advantages over borosilicate glasses. Glasses that we have studied include P_2O_5-Fe_2O_3-FeO glasses [4]; P_2O_5-Fe_2O_3 glasses doped with (SiO_2, B_2O_3, Al_2O_3) [5] and doped with (Li_2O, Na_2O, K_2O, MgO, CaO, BaO, PbO) [6] and P_2O_5-Fe_2O_3-Na_2O-Al_2O_3 [7] glasses. Mössbauer spectroscopy has been used to understand the oxidation states and local environment of iron which is an important component in all of these systems. Sulphate can be present at high levels in wastes. Bingham et al. confirmed that P_2O_5-Fe_2O_3-FeO glasses without modification to improve performance can make poor hosts for sulphate wastes [4]. Detailed studies were undertaken on the system P_2O_5–Fe_2O_3–FeO–R_xO_y where R = R^+, R^{2+}, R^{3+} and R^{4+}. Fitted CS and

QS were consistent with a range of distorted octahedral Fe sites and hyperfine parameters indicated that glass composition did not have a large effect on local environment of Fe^{2+} and Fe^{3+} cations. However, the redox ratio, $Fe^{2+}/\Sigma Fe$, was substantially affected by the abundance and type of modifier addition [5].

2.3 Non-nuclear waste vitrification

Several non-nuclear waste streams are now routinely incinerated, producing energy and reducing waste volume. Such wastes include sewage sludge, and incineration results in large amounts of sewage sludge ash (SSA) which can contain harmful and leachable components [1, 8, 9]. Ashes may require further treatment prior to disposal to render them inert or to enable their re-use in other applications. The oxidation state and structural properties of iron can vary substantially in vitrified SSA wastes and influences physical properties. Simulated SSA was vitrified and redox states and local environments of Fe within the samples have been investigated using ^{57}Fe Mössbauer spectroscopy and X-ray Absorption Spectroscopy. Analysis of spectra used three extended Voigt-based fitting (xVBF) profiles. The distribution of hyperfine parameters of two Fe^{3+} lineshapes suggests one represents tetrahedrally coordinated Fe^{3+} and one octahedrally coordinated Fe^{3+}. Variations in the Fe^{2+} parameters are, however, more marked and indicate multiple coordination environments. Mössbauer spectroscopy identified a preference for the redox reaction $Fe^{3+}_{tetrahedral} \leftrightarrow Fe^{2+}$ over reactions involving octahedral Fe^{3+} ions [8, 9].

2.4 Novel glass processing—microwave melting

Batch glass melting is a mature technology but it is energy intensive. Microwave heating has many advantages over conventional heating which include reduced energy consumption, very rapid heating rates ($>400\ °C\ min^{-1}$), reduced processing time and temperature, reduction in loss of volatile batch components, and prevention of undesirable decomposition or redox processes. A fundamental constraint of microwave heating is that a major constituent of the batch must be microwave absorbing [10]. Although most glass compositions used for HLW immobilisation [1, 4] require high processing temperatures, phosphate glasses have low melting temperatures, high solubility for transition metal oxides and exhibit equivalent or superior chemical durability to borosilicate systems. A glass with composition $40Fe_2O_3$-$60P_2O_5$ (mol%) was chosen to study the effect of melting route and choice of precursor on Fe redox state. Glasses were prepared by conventional melting using P_2O_5 and $NH_4H_2PO_4$ as phosphate precursors and Fe_2O_3 and Fe_3O_4 as iron precursors. Glasses containing Fe_3O_4 were also melted by microwave heating using a previously reported procedure [11]. Mössbauer spectra and parameters, analysed using Extended Voigt-based fitting (xVBF), are shown in Fig. 1. The Fe^{2+} / Fe^{3+} ratio varied with melting route and phosphate precursor. Irrespective of average valence of the starting precursor ($Fe_3O_4 – Fe^{2.67+}$; $Fe_2O_3 – Fe^{3+}$) all conventionally melted glasses had an average valence of $Fe^{2.9+}$. This suggested that equilibrium in these systems was reached after melting for 5 h at 1,150 °C. Microwaved glasses showed different average valence states which appeared to be dependent on phosphate precursor; for Fe_3O_4-P_2O_5 (M), $Fe^{2.63+}$ and for Fe_3O_4-ADP (M), $Fe^{2.568+}$. These

Glass	CS	QS	FWHM	Area	Site
	mm s^{-1}	mm s^{-1}	mm s^{-1}	%	
Fe$_3$O$_4$-ADP	0.41	0.82	0.16	57	Fe^{3+}
(M)	1.18	2.27	0.16	43	Fe^{2+}
Fe$_3$O$_4$-P$_2$O$_5$	0.41	0.83	0.13	73	Fe^{3+}
(M)	1.09	2.43	0.13	22	Fe^{2+}
Fe$_3$O$_4$-ADP	0.38	0.84	0.13	91	Fe^{3+}
(C)	1.06	2.42	0.13	9	Fe^{2+}
Fe$_3$O$_4$-P$_2$O$_5$	0.39	0.85	0.14	90	Fe^{3+}
(C)	1.01	2.49	0.14	10	Fe^{2+}
Fe$_2$O$_3$-ADP	0.39	0.83	0.13	90	Fe^{3+}
(C)	1.04	2.43	0.13	10	Fe^{2+}
Fe$_2$O$_3$-P$_2$O$_5$	0.38	0.87	0.15	90	Fe^{3+}
(C)	1.07	2.41	0.15	10	Fe^{2+}
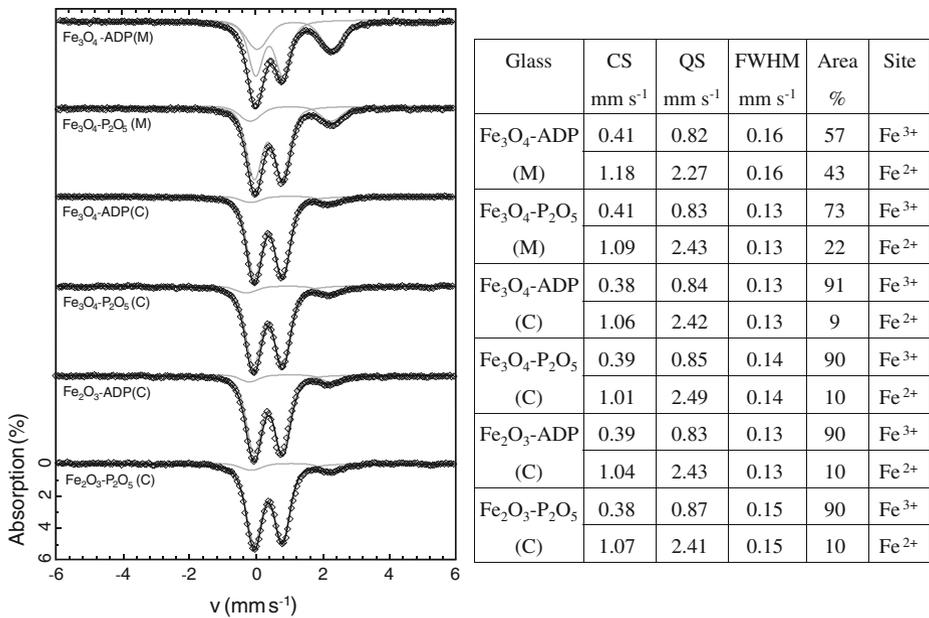
Fig. 1 Mössbauer spectra and parameters (±0.02 mm s^{-1}) for 40Fe$_2$O$_3$-60P$_2$O$_5$ (mol%) glasses formed by conventional heating (C) and microwave heating (M). Note: *ADP* ammonium dihydrogen phosphate, NH$_4$H$_2$PO$_4$

results demonstrate the feasibility of producing glasses by microwave heating. The differences between microwaved and conventionally melted glasses are attributed to short melting times stabilising non-equilibrium average valence states and the presence of NH$_3$, generated during decomposition of the NH$_4$H$_2$PO$_4$ precursor, creating a reducing environment.

2.5 Ceramic materials for waste immobilisation

Ceramics with pyrochlore or pyrochlore-related structures are promising candidates for the disposition of radionuclides. They couple excellent chemical durability and resistance to radiation damage with the ability to accommodate plutonium and minor actinides fractions of spent nuclear fuel [12]. Y$_2$TiO$_5$ and CaZrTi$_2$O$_7$ were studied to investigate the structural changes which occur during doping of these materials with Ce (as a Pu surrogate) and Fe (as a typical fuel cladding contaminant). Y$_2$TiO$_5$ (or Y$_{2.67}$Ti$_{1.33}$O$_{6.67}$) crystallises with a disordered cation-deficient pyrochlore structure where the Y and Ti cations adopt the unusual combination of 7- and 5-fold coordination respectively [13]. CaZrTi$_2$O$_7$ adopts a monoclinic structure where Ca and Zr cations are 8 and 7-fold coordinated and Ti cations sit in three different crystallographic sites, two which have 6-fold symmetry and one which has 5-fold symmetry. Samples in the (Ca$_{1-x}$Ce$_x$)Zr(Ti$_{2-2x}$Fe$_{2x}$)O$_7$ system were fabricated by solid state synthesis, from intimately mixed oxide and carbonate precursors heated at 1,300 °C for 8 h, in 0.1 interval steps of x. X-ray diffraction analysis confirmed that all samples in the range $0.0 \leq x \leq 0.4$ were single phase and adopted the monoclinic
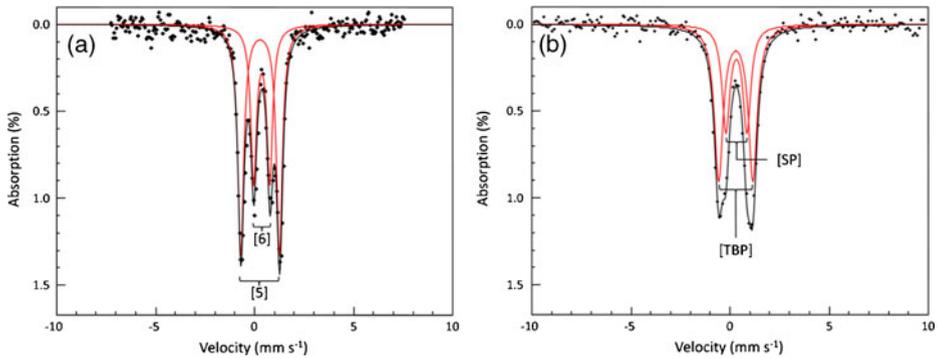
Fig. 2 **a** Mössbauer spectra for $(Ca_{0.6}Ce_{0.4})Zr(Ti_{1.2}Fe_{0.8})O_7$. [5] and [6] indicate doublets corresponding to five- and six-fold coordinated iron. **b** Mössbauer spectra for $(Y_{1.7}Ce_{0.3})(Ti_{1.7}Fe_{0.3})O_5$. [SP] and [TBP] indicate doublets corresponding to iron in square pyramidal and trigonal bipyramidal geometry

Table 1 Mössbauer parameters (± 0.02 mm s^{-1}) for $(Ca_{1-x}Ce_x)Zr(Ti_{2-2x}Fe_{2x})O_7$ ceramic

Composition (x)	CSmm s^{-1}	QS mm s^{-1}	FWHM mm s^{-1}	Area %	Site
0.1	0.27	2.16	0.19	81	[5]
	0.31	0.80	0.22	19	[6]
0.2	0.28	2.05	0.18	78	[5]
	0.36	0.77	0.19	22	[6]
0.3	0.28	1.97	0.19	69	[5]
	0.36	0.77	0.17	31	[6]
0.4	0.28	1.91	0.21	60	[5]
	0.36	0.77	0.20	40	[6]

structure. For x values greater than 0.4, samples were multiphase which made deconvolution of individual contributions in Mössbauer spectra difficult, therefore only single phase samples (x ≤ 0.4) were analysed. The spectrum obtained from x = 0.4 is shown in Fig. 2a. Two Lorentzian doublets were fitted to the data consistent with the presence of two distinct Ti/Fe sites with different environments. Parameters of the less intense doublet, Table 1, were consistent with $^{[6]}Fe^{3+}$. The larger doublet, was therefore inferred to be due to the presence of five-fold coordinate trigonal bipyramidal iron. Parameters are consistent with those reported by Berry et al. [14] and lower symmetry sites are characterised by larger quadrupole splitting. Table 1 shows that the iron preferentially partitions to the [5] coordinated site and the absence of any Fe^{2+} in the samples is consistent with processing in air. Samples were also prepared in the $(Y_{2-x}Ce_x)(Ti_{1-x}Fe_x)O_5$ (0.1 ≤ x ≤ 0.3) system by heating mixed precursors at 1,400 °C for 8 h. Ln_2TiO_5 type cation deficient pyrochlores adopt a number of different structures depending on composition and processing conditions [15]. The titanium cations adopt different 5-coordinate environments; square pyramidal (SP) in the orthorhombic and trigonal bipyramidal (TBP) in the hexagonal structure. XRD showed samples were multiphase containing both hexagonal and orthorhombic structured phases. Mössbauer spectra for x = 0.3 confirmed the presence of two Fe environments in the sample, Fig. 2b. The doublet with the larger QS was attributed to Fe in TBP as the parameters were similar to

Table 2 Mössbauer parameters (± 0.02 mm s^{-1}) for $(Y_{1.7}Ce_{0.3})(Ti_{1.7}Fe_{0.3})O_5$ ceramic

Composition (x)	CS mm s^{-1}	QS mm s^{-1}	FWHM mm s^{-1}	Area %	Site
0.3	0.30	1.72	0.27	62	[TBP]
	0.34	1.06	0.24	38	[SP]

[SP] and [TBP] indicate doublets corresponding to iron in square pyramidal and trigonal bipyramidal geometry
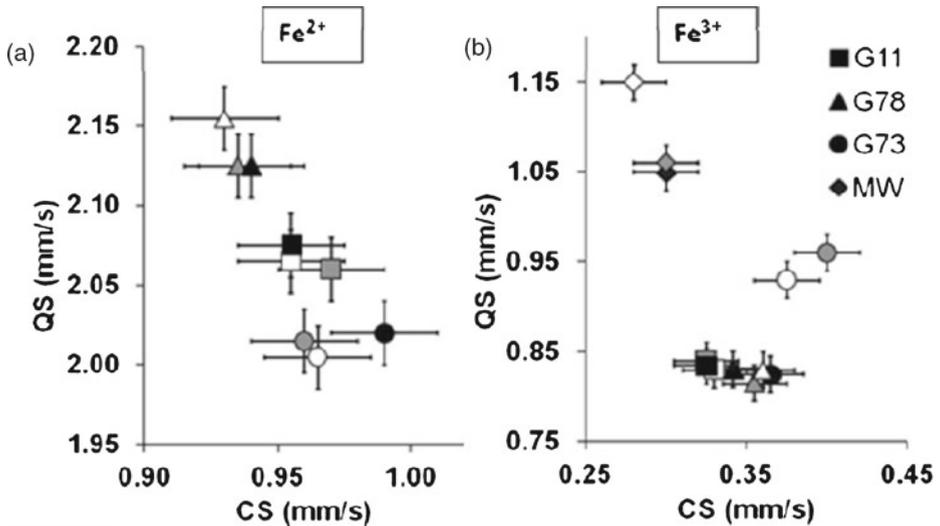
Fig. 3 Comparison of CS and QS for Fe^{2+} and Fe^{3+} in 0 MGy (*white*) and γ-irradiated 4 (*grey*) and 8 MGy glasses (*black*). Errors are from standard deviation of results associated with fitting of 3 experiments

those observed in the $(Ca_{1-x}Ce_x)Zr(Ti_{2-2x}Fe_{2x})O_7$ system. The other doublet was therefore inferred to be due to Fe in SP geometry and the Mössbauer parameters, Table 2, are consistent with those observed for Fe^{3+} in SP geometry in cuprate superconductors [16, 17].

2.6 Irradiation effects in glasses

Glasses for the immobilisation of nuclear waste can be expected to be exposed to a considerable dose of γ radiation over the life span of a wasteform. Four different glasses were exposed to a range of gamma radiation doses in order to explore the effect of radiation on the Fe oxidation and coordination. Glass frits of desired compositions were used to vitrify simulant wastes. Three alkali-borosilicate wasteforms (G11, G78 and MW) and one alkaline-earth alkali borosilicate wasteform (G73) were studied. The Fe_2O_3 content of these glasses varied from 5.2 mol% in G11 to 2.9 and 3.4 mol% in G73 and MW. The wastes vitrified in G11, G73 and G78 glasses contained reducing organic material. Samples and a control sample were dosed with 0, 4 and 8 MGy of gamma irradiation using a ^{60}Co source and studied by Mössbauer spectroscopy. Spectra were fitted with two Lorentzian doublets corresponding to Fe^{2+} and Fe^{3+}. No significant change was observed in Fe oxidation state between

the control sample and irradiated samples. This was consistent with results from a previous study [18]. Average CS and QS for Fe^{2+} in all samples, Fig. 3, showed no significant change with irradiation. Similarly the Fe^{3+} environments of samples G11 and G78 also showed no variation in response to radiation dose. Samples MW and G73 both showed statistically significant decreases in $QS(Fe^{3+})$ (0.10 ± 0.02 mm/s) at 4 MGy dose for MW, and (0.11 ± 0.02 mm/s) at 8 MGy for G73, consistent with Eissa et al. [18], in irradiated Na-borosilicate glasses. These shifts in $QS(Fe^{3+})$ indicate [4]Fe^{3+}/[6]Fe^{3+} increases [19]. This information, alongside other results [20] indicates that a mechanism initially proposed by Debnath et al. [21] and suggested by Brown et al. [22] for the remediation of gamma radiation induced defects (e$^-$, electrons, h$^+$, holes) occurred in these samples Eq. 1.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad Fe^{2+} + h^+ \rightarrow Fe^{3+} \tag{1}$$
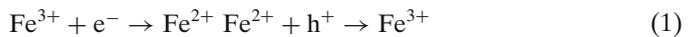
3 Conclusion

Mössbauer spectroscopy is valuable in providing information about the environment of iron in materials developed to store wastes. This knowledge informs the understanding of the materials' properties which must be controlled for the required stability. Future challenges include the study of vitrified materials to immobilise wastes containing the problematic actinide plutonium.

References

1. Donald, I.W.: Waste Immobilization in Glass and Ceramic Based Hosts: Radioactive, Toxic and Hazardous Wastes. Wiley, Chichester (2010)
2. Rancourt, D.G., Lagarec, K.: Recoil, Mössbauer Spectral Analysis Software for Windows (1998), described at http://www.kfki.hu/~mixhp/doc/pro/recoil.txt
3. Cassingham, N.J., Bingham, P.A., Hand, R.J., Forder, S.D.: Glass Technol.: Eur. J. Glass Sci. Technol. A **49**, 21–26 (2008)
4. Bingham, P.A., Hand, R.J., Forder, S.D., Lavaysierre, A., Kilcoyne, S.H., Yasin, I.: Mater. Lett. **60**, 844–847 (2006)
5. Bingham, P.A., Hand, R.J., Forder, S.D.: Mater. Res. Bull. **41**, 1622–1630 (2006)
6. Bingham, P.A., Hand, R.J., Hannant, O.M., Forder, S.D., Kilcoyne, S.H.: J. Non-Cryst. Solids **355**, 1526–1538 (2009)
7. Bingham, P.A., Forder, S.D., Hand, R.J., Lavaysierre, A.: Hyperfine Interact. **165**, 135–140 (2005)
8. Hannant, O.M., Bingham, P.A., Forder, S.D., Hand, R.J., Glass Technol.: Eur. J. Glass Sci. Technol. A **49**, 27–32 (2008)
9. Hannant, O.M., Forder, S.D., Bingham, P.A., Hand, R.J.: Hyperfine Interact. **192,** 47–42 (2009)
10. Rao, K.J., Vaidhyanathan, B., Ganguli, M., Ramakrishnan, P.A.: Chem. Mater. **11**, 882 (1999)
11. Stennett, M.C., Hyatt, N.C.: Mat. Res. Soc. Symp. Proc. **1124**, 147–152 (2009)
12. Ewing, R.C., Weber, W.J., Lian, J.: J. Appl. Phys. **95**, 5949 (2004)
13. Mumme, W.G., Wadsley, A.D.: Acta. Cryst. B **24**, 1327 (1968)
14. Berry, F.J., Lumpkin, G.R., Oates, G., Whittle, K.R.: Hyperfine Interact. **166**, 363 (2005)
15. Shlyakhtina, A.V., Belov, D.A., Karyagina, O.K., Shcherbakova, L.G.: J. Alloys Compd. **479**, 6 (2009)
16. Akachi, T., Escamilla, R., Marquina, V., Jimenez, M., Marquina, M.L., Gomez, R., Ridaura, R., Aburto, S.: Physica C **301**, 315 (1998)
17. Gomez, R., Marquina, V., Arevalo, A., Perez, J.L., Ridaura, R., Marquina, M.L., Escamilla, R., Akachi, T.: Hyperfine Interact. **171**, 293 (2006)

18. Eissa, N.A., Sheta, N.H., El-Meligy, W.M., El-Minyawi, S.M., Sallam, H.A.: Rad. Phys. Chem. **44**, 35 (1994)
19. Darby-Dyar, M., Agresti, D.G., Schaefer, M.W., Grant, C.A., Sklute, E.C.: Ann. Rev. Earth Planet Sci. **34**, 83 (2006)
20. McGann, O., Bingham, P., Hand, R., Kavčič, M., Bučar, K., Edge, R., Hyatt, N.C.: J. Nucl. Mater **429**, 353 (2012)
21. Debnath, R.: J. Mater. Res. **16**, 127 (2001)
22. Brown, G.: J. Mater. Sci. **10**, 1841 (1975)