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Nanosized magnetite formation in Fe-containing glass

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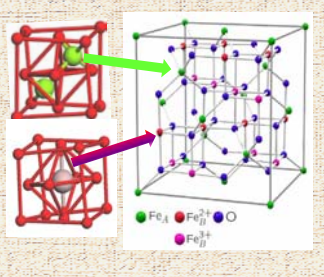
We present the preparation and structural properties of a series of Fe-containing borosilicate glasses as a function of the ratio SiO_2/Fe_2O_3 which is ranging from 1.49 to 2.68. The role of nucleators (Cr_2O_3 and P_2O_5) was also investigated. X-Ray diffraction has revealed the formation of magnetite as the major or unique crystalline phase whereas Mössbauer spectroscopy revealed the the additional presence of a large amount of Fe-rich paramagnetic phases. We discuss the role of the nucleators and intermediants (Al_2O_3 and MgO) on the disorder in both tetrahedral and octahedral sites of the magnetite.

Magnetic vitroceramics

Vitroceramics: vitreous matrix containing dispersed nanograined crystalline phase.
Crystalline grains nucleate and grow:
- during cooling down of the molten composition
- as a result of different thermal treatments

Very flexible and cheap process that depends on:
- appropriate choice of the ingredients
- particular thermal excursion

Vitroceramics containing magnetic nano-crystallite (iron oxides, barium, and srontium hexaferrites) provides
- very fine single- or multi-domain particles
- superparamagnetic behavior
- dipol-dipol interaction prevents grain aglomeration



Magnetite: Fe_3O_4

-Inverse spinel structure:
Fe^{3+}_A Tetrahedral positions
Fe^{3+}_B & Fe^{2+}_B octahedral positions
-Continuous exchange of electrons between Fe^{2+} and Fe^{3+} in the octahedral positions
-Verwey transition at T_V~120 K
Still under dispute:
Charge & orbital ordering
Multiferroicity

Sample preparation

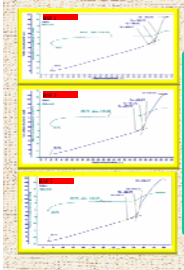
Basically: borosilicatic glass with constant B_2O_3 and Na_2O contentnd small amounts of either one of Al_2O_3, MgO, and nucleators (Cr_2O_3, P_2O_5).
Variation of the ratio SiO_2/Fe_2O_3.
The batches where melt into alumina crucible for 2.5-3 hours in the temperature range 1400-1500 °C.
-The melts were poured onto a steel sheet and the resulting slabs were immediately transferred to an annealer operating at 560 °C for 2-4 hours.
--Cooling down 450 °C (10 °C/hour)
-Cooling down to 300 °C (20 °C/hour) and then inertially to 25 °C.

Sample code	Oxide composition (%w)							
	SiO_2	B_2O_3	Na_2O	Fe_2O_3	Cr_2O_3	Al_2O_3	MgO	P_2O_5
BSF1	47	28.6	6.4	17.5	0.5	-	-	
BSF2	45.6	28.6	6.4	17.5	0.5	1.1	0.3	-
BSF3	46.5	28.6	6.4	17.5	-	-	-	1
BSF4	36.5	28.6	6.4	24.5	0.5	3.5	-	-
BSF5	39.5	28.6	6.4	24.5	-	-	-	1

Why this compositions?

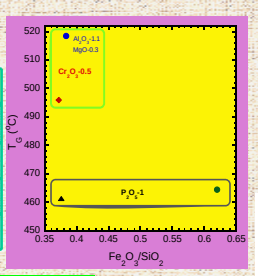
- Cr in melt: Cr^{2+} and Cr^{6+} . The latter is stabilized by the presence of alkaline oxides (Na). Cr^{6+} has an intense field q/r = 17.2 with a strong ordering effect on O ions. Promotes the separation of crystalline nuclei at low T.
- P^{5+} in tetrahedral coordination: the charge difference between Si^{4+} ad P^{5+} leads to separation of P in combination with alkaline metal
- AlO_4 stabillizes PO_4 tetrahedra due to the special bonds, so, increases the stability of glass relative to recrystallization.

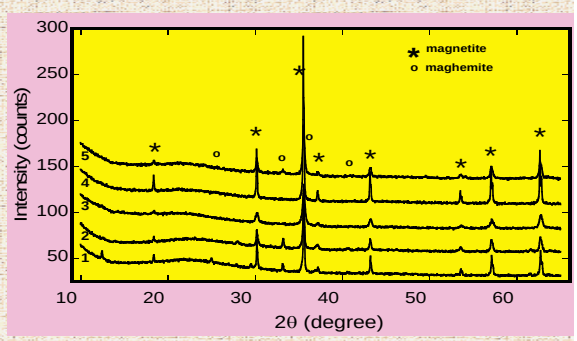
1. Fe ion in glass melt: Fe^{3+} and Fe^{2+}
2. In oxidizing environment, in glass melt: $4Fe^{3+} + 2O \rightleftharpoons 4Fe^{2+} + O_2$
   - Fe^{3+} enters tetrahedral coordination (FeO_4), Fe^{2+} enters octahedral coordination (FeO_6)
3. Magnetite: appropriate concentration of both Fe^{3+} and Fe^{2+}
4. Fe^{3+} in tetrahedral coordination: FeO_4 competes with AlO_4
5. Fe^{2+} in octahedral coordination: FeO_6 competes with MgO_6



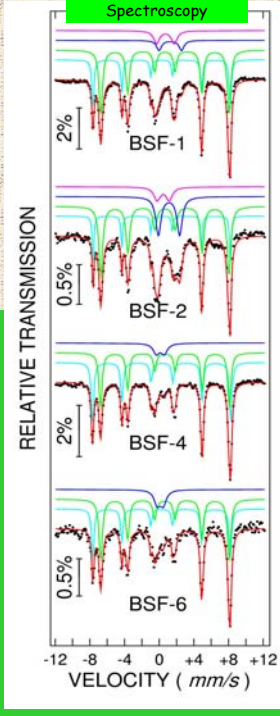
Thermal expansion

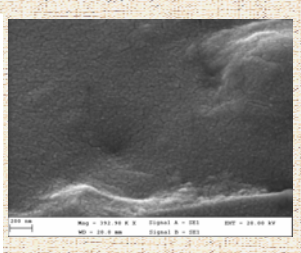
Sample	T_{ir}	T_G	T_{sr}	T_D
BSF 1	464.8	495.9	509.5	553.6
BSF 2	484.1	518.4	532.8	577.4
BSF 3	425.5	461.2	474	572.4
BSF 5	419.2	464.4	479.1	546.8

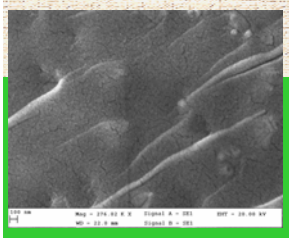


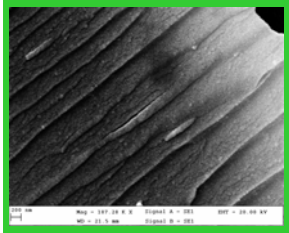


Mössbauer Spectroscopy

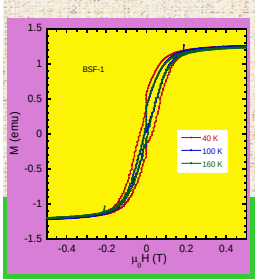


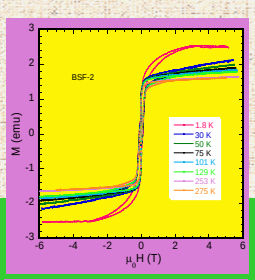


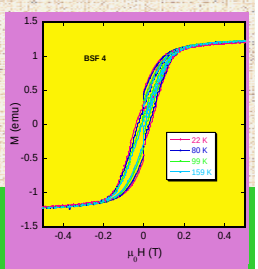


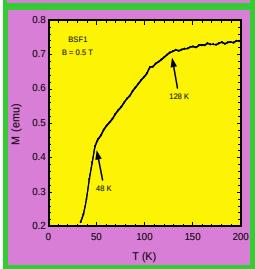


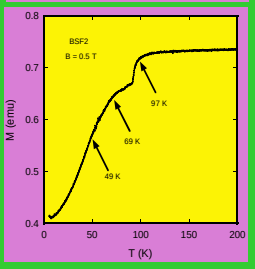
Magnetic Response

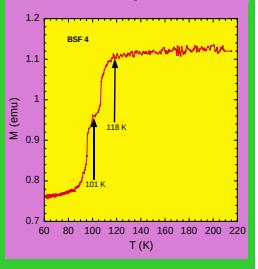












Acknowledgments

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BSF1: R=2.1(1), close to stoichiometric magnetite.
BSF2: R=3.3 -sites A less occupied.
BSF4: R=1.1- sites B less occupied, mainly Fe^{2+}.
BSF6: R=1.7- sites B less occupied, empty sites equally distributed to both Fe^{2+} and Fe^{3+}.
All samples shows paramagnetic phases dispersed in the glass matrix