

## **Mechanism of Phase Formation in the Batch Mixtures for Slag-Bearing Glass Ceramics - 12207**

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### **ABSTRACT**

Slag surrogate was produced from chemicals by heating to 900 °C and keeping at this temperature for 1 hr. The product obtained was intermixed with either sodium disilicate (75 wt.% waste loading) or borax (85 wt.% slag loading). The mixtures were heat-treated within a temperature range of 25 to 1300 °C. The products were examined by X-ray diffraction and infrared spectroscopy. The products prepared at temperatures of up to 1000 °C contained both phase typical of the source slag and intermediate phases as well as phases typical of the materials melted at 1350 °C such as nepheline, britholite, magnetite and matrix vitreous phase.

### **INTRODUCTION**

Solid radioactive waste such as incinerator slag needs to be consolidated and transformed into stable chemically durable form suitable for long-term storage or final disposal. One of the most promising methods of solid waste processing is vitrification [1]. We have proposed sodium disilicate ( $\text{Na}_2\text{Si}_2\text{O}_5$ ) and sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) as glass forming additives and studied in details the structure and leachability of the glass crystalline materials produced in a lab-scale furnace and determined compositions suitable as waste forms [1-3]. Understanding the steps of the vitrification process may provide for optimization of its conditions (decrease of process temperature or increase of reactions rate). This paper describes the results of this work.

### **EXPERIMENTAL**

Mixture of reagent-grade chemicals  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{SiO}_2$ , and  $\text{Sm}_2\text{O}_3$  was calcined at 1000 °C for 6 h to obtain an incinerator slag surrogate with a target composition of (wt.%) 6.0  $\text{Na}_2\text{O}$ , 9.0  $\text{K}_2\text{O}$ , 15.0  $\text{CaO}$ , 15.0  $\text{Al}_2\text{O}_3$ , 10.0  $\text{FeO}$ , 30.0  $\text{SiO}_2$ , 10.0  $\text{P}_2\text{O}_5$ , 5.0  $\text{Sm}_2\text{O}_3$  (trivalent actinides surrogate). Thus produced simulated slag was intermixed with either liquid sodium silicate (soluble glass) with approximate composition  $\text{Na}_2\text{Si}_2\text{O}_5$  or  $\text{Na}_2\text{B}_4\text{O}_7$  (borax) at mass ratios: 75 Slag, 25  $\text{Na}_2\text{Si}_2\text{O}_5$  and 85 Slag, 15  $\text{Na}_2\text{B}_4\text{O}_7$ . Batches were heat-treated in silicon carbide crucibles in a resistive furnace at temperatures of 500 °C, 700 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C with keeping at each temperature for 1 h.

The products were examined by X-ray diffraction (XRD) using a Rigaku D/Max 2200 diffractometer (Cu  $K_\alpha$  radiation, voltage is 40 keV, current is 20 mA) and scanning micro-infrared reflectance spectroscopy using a Perkin Elmer Spectrum One unit equipped with an AutoImage microscope.

The data were compared with those obtained for the products with same chemical composition but melted at 1350 °C [3] and reference XRD patterns [4].

## RESULTS

### Silicate-based materials

XRD patterns of the samples produced at various temperatures with sodium disilicate flux are shown on Fig. 1. The slag surrogate was composed of vitreous phase, unreacted or altered quartz ( $\text{SiO}_2$ ), samarium oxide ( $\text{Sm}_2\text{O}_3$ ), sodium-calcium phosphate and silicophosphate phases with variable chemical composition and minor spinel structure phase. The batches composed of slag surrogate and sodium disilicate and heat treated at temperatures of up to 1000 °C contained  $\alpha$ -quartz being a phase occurred in the slag surrogate. The batches heat-treated at 500 and 700 °C still contained minor sodium-calcium phosphate with approximate  $\text{NaCaPO}_4$  composition and trace of unreacted or altered samarium oxide and magnetite-type spinel. At the temperatures over 700 °C sodium-calcium phosphate reacts with silica yielding complex silicophosphates with rather low  $\text{P}_2\text{O}_5$  content –  $\text{Ca}_2\text{SiO}_4 \cdot (0.05 \div 0.5) \text{Ca}_3(\text{PO}_4)_2$  where Sm enters as an isomorphous dopant.

Silicophosphate was found to be major phase in the sample heat-treated at a temperature of 1000 °C and nearly the only phase in the samples heat-treated at 1100, 1200 and 1300 °C. All these samples were partly melted sinters.

These sinters were studied in more details by scanning infrared reflectance spectroscopy (Fig. 2). All the samples even produced at 1200 °C were structurally inhomogeneous as it is seen from significant variations in position of reflection bands especially within the range of 1000-1300  $\text{cm}^{-1}$ . Some bands are split into several components and may be attributed to various crystalline phases. Broad structureless bands are due to vitreous phase with widely variable chemical composition and black grains, probably magnetite. The bands with maxima at 1150-1200  $\text{cm}^{-1}$  are due to vibrations of Si—O bonds in  $[\text{SiO}_4]$  tetrahedra with high degree of connectedness (four –  $\text{Q}^4$  and three –  $\text{Q}^3$  bridging oxygen ions) [5,6] in the structure of quartz and silicophosphates. The bands with maxima at 1200-1250  $\text{cm}^{-1}$  are due to vibrations of P—O bonds in  $[\text{PO}_4]$  tetrahedra in the structure of phosphates and silicophosphates. Some spectra contain both them and may be assigned to silicophosphates.

As seen from IR spectra of the samples (Fig. 2) increase of heat-treatment temperature results in reduction in intensity of the broad band at 3000-3600  $\text{cm}^{-1}$  and narrower band at 1400-1800  $\text{cm}^{-1}$  due to stretching and bending modes in the molecules of structurally bound or absorbed water and OH groups and higher degree of similarity of the spectra within the same sample demonstrating its homogenization.

The sample produced by melting at 1350 °C and pouring onto a metal plate (quenched) was composed of predominant vitreous phase and minor nepheline. Traces of silicophosphate and magnetite-type spinel were also present [3]. In the sample slowly cooled in turned-off furnace (annealed) nepheline was found to be major phase whereas spinel and silicophosphate (britholite-type) were minor phases.

Thus silicophosphate was a phase formed during heat-treatment of the batches whereas nepheline crystallized from the melt. As seen from Fig. 1 melted and quenched sample contains trace of the silicophosphate phase therefore major fraction of this phase is also a product of crystallization from the melt. Re-crystallization changes chemical composition of this phase and its nature yielding a britholite-type phase with average crystal chemical formula  $(\text{Na}_{2.82}\text{K}_{0.68}\text{Ca}_{2.04}\text{Fe}_{2.57}\text{Al}_{1.72}\text{Sm}_{0.17})(\text{Si}_{4.52}\text{P}_{0.70}\text{Al}_{0.78})\text{O}_{26-x}$  [3].

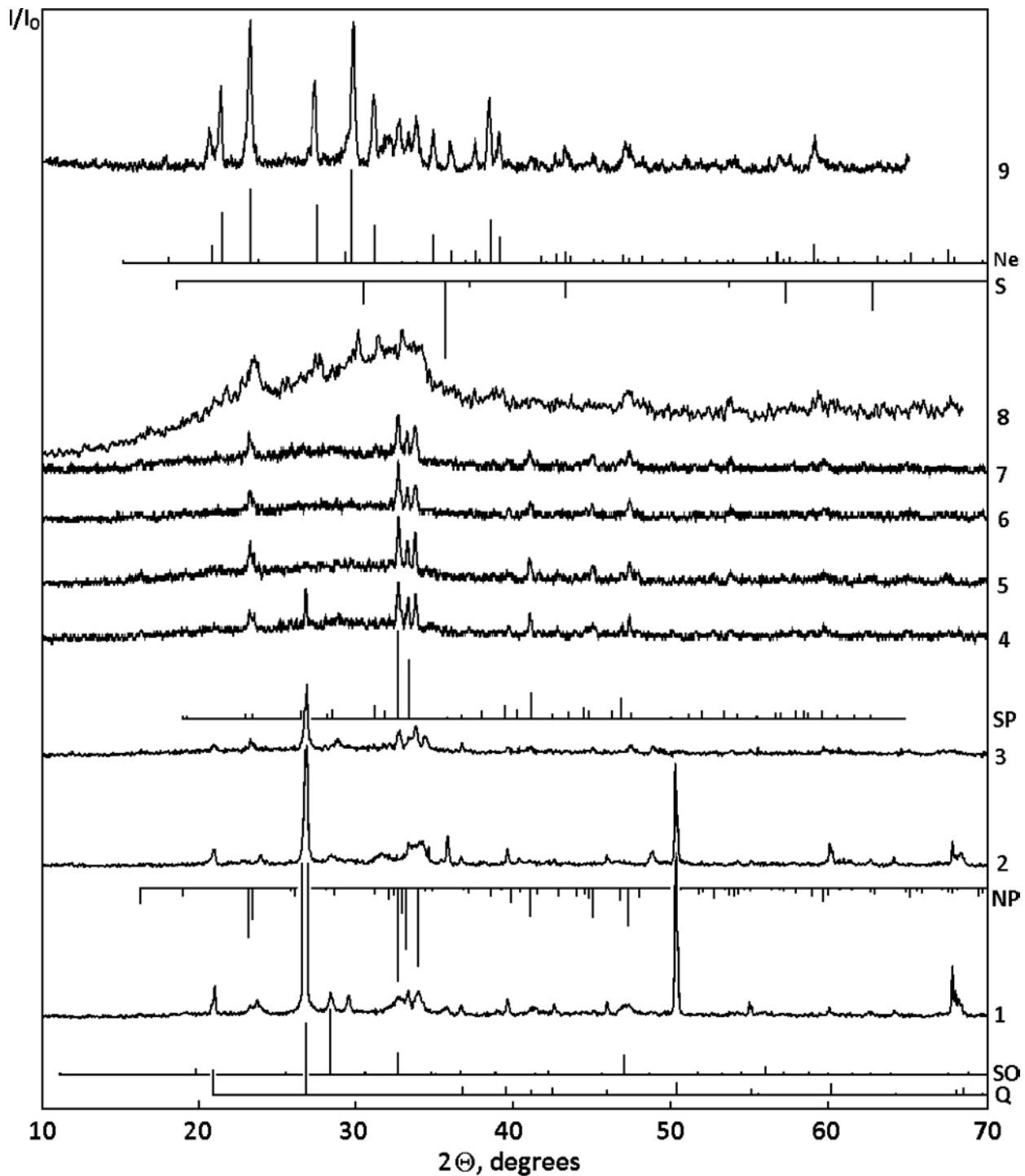


Fig. 1. XRD patterns of the slag-bearing samples produced with sodium disilicate flux at 500 (1), 700 (2), 900 (3), 1000 (4), 1100 (5), 1200 (6), 1300 °C (7), and melted at 1350 °C and quenched (8) or slowly cooled (9) and reference compounds:  $\alpha$ -quartz (Q), Sm<sub>2</sub>O<sub>3</sub> (SO), NaCaPO<sub>4</sub> (NP), calcium silicophosphate (SP), nepheline (Ne).

## Borosilicate-based materials

XRD patterns of the samples produced at various temperatures with sodium tetraborate flux are shown on Fig. 3. The batch heat-treated at 500 °C is composed of the phases typical of source slag surrogate: quartz, sodium phosphate, minor unreacted samarium oxide and magnetite-type spinel. At higher temperatures the ratio between sodium-calcium phosphate and britholite-type silicophosphate changes in favor of the second phase due to reaction between phosphate, silica and samarium oxide. All the  $\text{Sm}_2\text{O}_3$  has completely reacted by a temperature of 700 °C. Nepheline formed at temperatures over 700 °C – most actively above 900 °C but both in the partly melted sinter produced at 1300 °C and in the melted at 1350 °C and quenched or annealed materials it remained secondary abundant phase as compared to britholite-type silicophosphate. In the whole, phase formation reactions in the batches were mostly completed by 1000 °C.

Figure 4 shows that the products even after heating at a temperature of 900 °C were rather uniform. Because major process runs by a mechanism of dissolution of source slag surrogate constituents in low viscous sodium borate melt most of analytical points on Fig. 4 correspond to vitreous phase. Broad band at  $3000\text{-}3600\text{ cm}^{-1}$  and narrower band at  $1400\text{-}1800\text{ cm}^{-1}$  are due to stretching and bending modes in the molecules of structurally bound or absorbed water and OH groups in complex compounds. These bands disappeared within the temperature range between 900 and 1000 °C. Within the wavenumber range of the bands due to vibrations in the boron-, silicon-, phosphorus-oxygen and complex groups the bands with maxima at  $1450\text{-}1500$ ,  $1100\text{-}1200$ , and  $700\text{-}800\text{ cm}^{-1}$  were present. The bands at  $1300\text{-}1500\text{ cm}^{-1}$  are due to vibrations of B—O bonds in  $[\text{BO}_3]$  triangles in complex diborate and tetraborate groups. The bands at  $1100\text{-}1200\text{ cm}^{-1}$  are due to superposition of stretching modes of B—O bonds in  $[\text{BO}_4]$  tetrahedra in tetraborate groups and Si—O bonds in  $[\text{SiO}_4]$  tetrahedra in quartz and quartz-like fragments in the source slag surrogate. The band at  $700\text{-}800\text{ cm}^{-1}$  is due to bending modes in borate groups [5-7]. As seen from Fig. 4 chemical composition the material heat-treated at 900 °C in various analytical points is some variable: both areas enriched with boron-oxygen and silicon-oxygen constituents with various degree of connectedness occur.

The products produced at higher temperatures have similar phase composition and microstructure. The spectra of the product heat-treated at 1300 °C in some analytical points are characterized by splitting of the bands due to crystallization and segregation of the britholite-type and nepheline phases. In other points spectra are typical of glass and these points correspond to vitreous phase.

## DISCUSSION

Phase formation reactions in the batches of the slag-bearing materials produced with sodium tetraborate flux were completed at lower temperatures as compared to reactions in the system with sodium disilicate flux even at some higher slag loading in the materials. Unlike the system with sodium tetraborate flux where mechanism of phase formation is close to simple dissolution of slag constituents in low viscous borate melt, in the system with sodium disilicate the phase formation process runs through formation of intermediate phases following by melting and re-crystallization with segregation of different major phase distinct from formed at previous stages of the phase formation process. Reactions in the slag-bearing silicate-based mixtures were mostly completed by 1000 °C but higher temperatures were required to dissolve residual quartz and homogenize the melt.

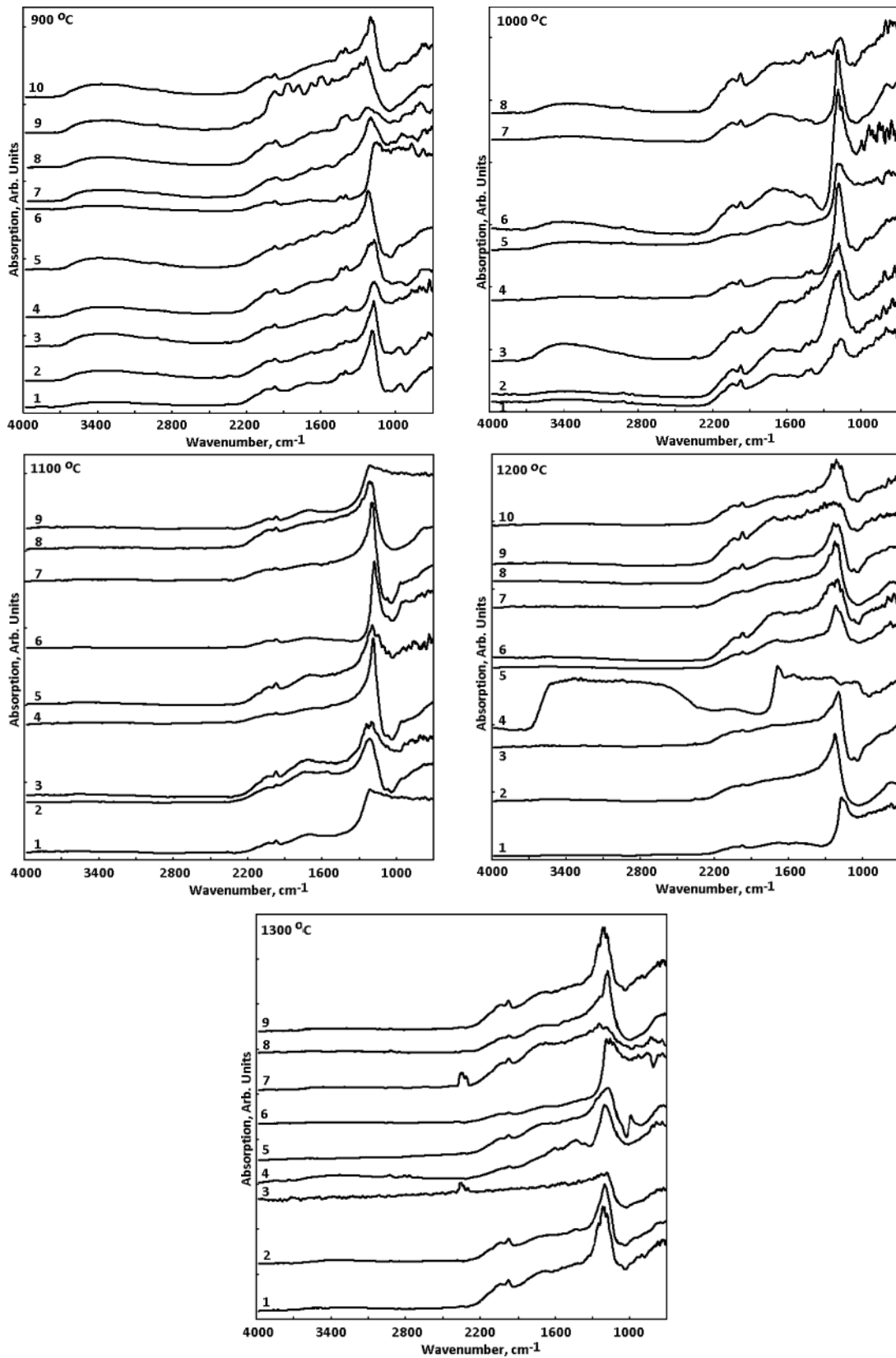


Fig. 2. IR reflectance spectra of the samples with sodium disilicate flux sintered at various temperatures (digits are analytical points).

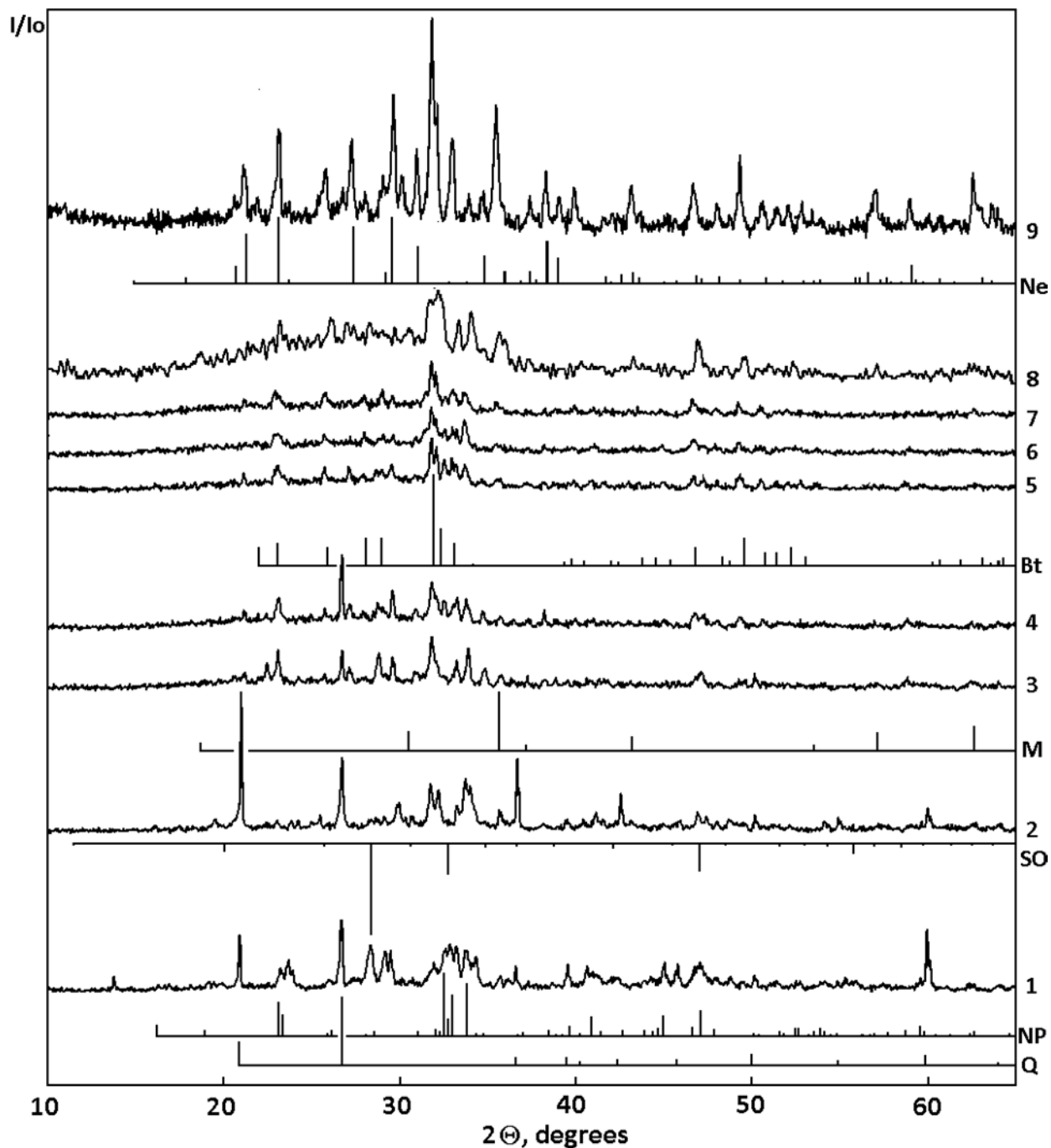


Fig. 3. XRD patterns of the slag-bearing samples produced with sodium tetraborate flux at 500 (1), 700 (2), 900 (3), 1000 (4), 1100 (5), 1200 (6), 1300 °C (7), and melted at 1350 °C and quenched (8) or slowly cooled (9) and reference compounds:  $\alpha$ -quartz (Q),  $\text{Sm}_2\text{O}_3$  (SO),  $\text{NaCaPO}_4$  (NP), calcium silicophosphate close to britholite (Bt), nepheline (Ne), magnetite (M).

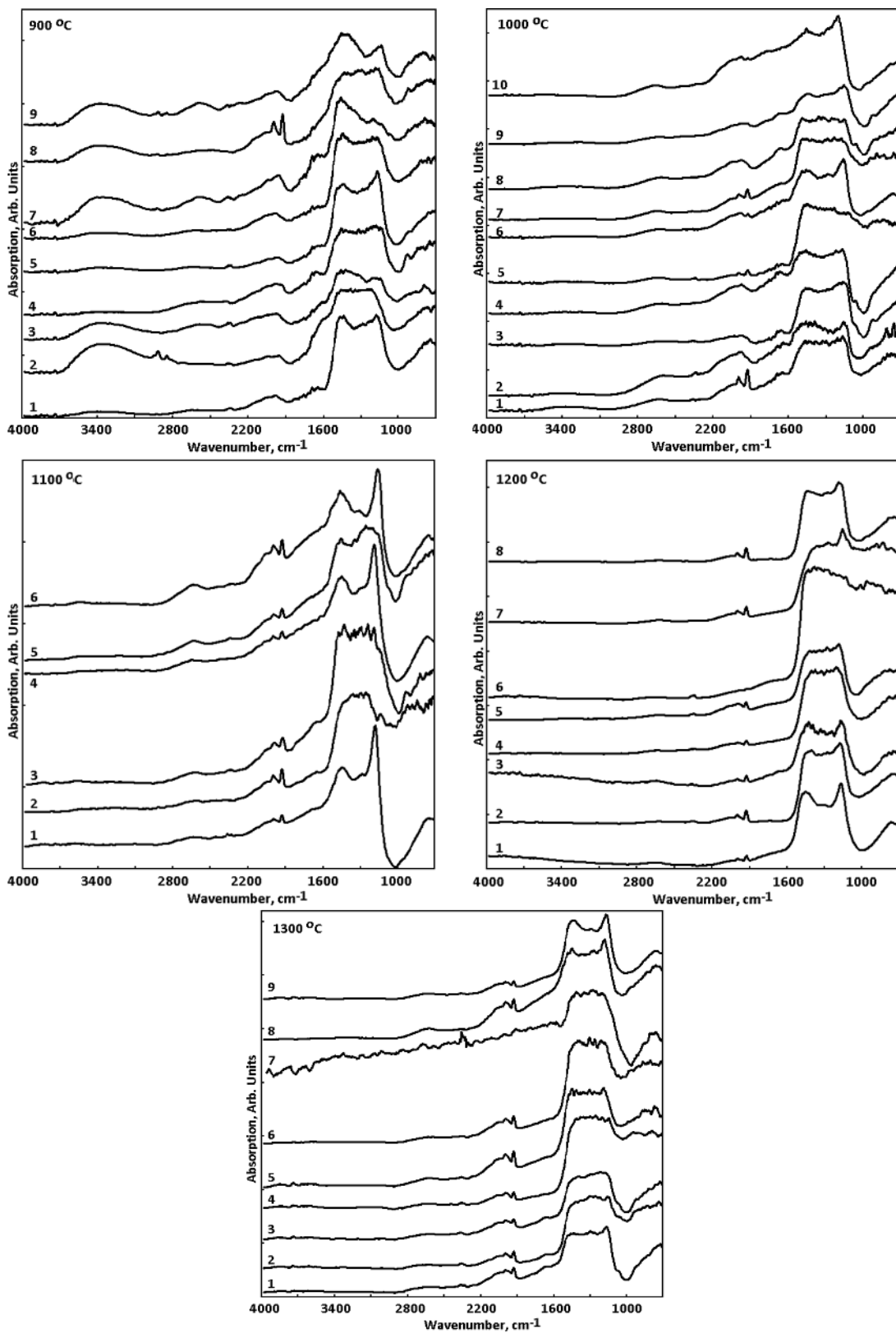


Fig. 4. IR reflectance spectra of the samples with sodium tetraborate flux sintered at various temperatures (digits are analytical points).

Materials produced with sodium tetraborate flux have at the same temperature much more uniform microstructure as compared to those produced with sodium disilicate flux. In the borate-based materials the silicophosphate phases both occurred in the source slag surrogate and formed at early stages of heat-treatment remained right up till melting and segregated during melt cooling.

Samarium used as a trivalent actinides ( $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ) surrogate was not (or just partly) incorporated in the structure of the source slag surrogate. In the system with sodium disilicate flux  $\text{Sm}_2\text{O}_3$  has reacted completely only at temperatures between 900 and 1000 °C. In the system with sodium tetraborate flux no  $\text{Sm}_2\text{O}_3$  reflections were observed on XRD pattern of the sample heat-treated at 700 °C. At that  $\text{Sm}_2\text{O}_3$  may be either dissolved in initial melt or enters the britholite-type silicophosphate phase which was kept at higher temperatures and segregated from the melt at its cooling. Behavior of trivalent actinide oxides is expected to be similar.

## CONCLUSION

Vitrification process in batch mixtures consisting of slag surrogate and either sodium disilicate or sodium tetraborate runs through formation of intermediate phases mainly silicophosphates capable to incorporate Sm as trivalent actinides surrogate. Reactions in the batch mixtures are in the whole completed by ~1000 °C but higher temperatures are required to homogenize the products. If in the borate-based system the mechanism is close to simple dissolution of slag constituents in the low viscous borate melt, then in the silicate-based system the mechanism was found to be much complicated and includes re-crystallization during melting with segregation of newly-formed nepheline type phase.

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