

HIGH-TEMPERATURE REACTIONS OF SODIUM CHROMATE WITH SILICA

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Reactions between sodium chromate and silica were studied on mixtures of silica sol with chromate solutions. After thermal exposure the conversion degree was determined by chemical analysis and gas chromatography. The reaction products were identified by X-ray diffraction and optical microscopy. The mixtures were found to react at temperatures above 900 °C in two stages: the ternary compound $\text{NaCrSi}_2\text{O}_6$ (kosmochlor) forms at lower temperatures and above 1050 °C decomposes to Cr_2O_3 , $\text{Na}_2\text{Si}_2\text{O}_5$ and silica.

INTRODUCTION

In the previous study [1] it was shown that in agreement with thermodynamic prediction, mixtures of alkali chromates with silica combine at high temperatures, forming crystalline Cr_2O_3 (eskolaite) and alkali silicate. However, X-ray diffraction showed that in a lower temperature region there also arises, apart from eskolaite, another mineral originally called kosmochlor and later renamed to ureyite and having the composition $\text{NaCrSi}_2\text{O}_6$. Kosmochlor (ureyite) is a monoclinic mineral of green colour of the group of pyroxenes, and was originally discovered in meteorites. It is isostructural with $\text{NaAlSi}_2\text{O}_6$ (jadeite). X-ray structural data of this mineral are specified in the PDF2 database under the name kosmochlor [2]. C. Frondel and C. Klein [3] published X-ray data of an artificial mineral prepared by fusion of a non-stoichiometric mixture of SiO_2 , Na_2SiO_3 and Cr_2O_3 at 1100 °C and subsequent slow cooling down of the product. Well developed crystals up to 0.1 mm in size were obtained by fusing stoichiometric $\text{NaCrSi}_2\text{O}_6$ in mixture with Na_2SiO_3 in a 10:1 ratio at 1100 °C. Fusion of $\text{NaCrSi}_2\text{O}_6$ without extra SiO_2 and Na_2O yielded a product containing Cr_2O_3 and a vitreous phase.

According to the above mentioned authors, the phase relations in the system Cr_2O_3 - SiO_2 - Na_2O appear to be similar to those in the system Fe_2O_3 - SiO_2 - Na_2O in the sense that the two compounds $\text{NaFeSi}_2\text{O}_6$ (acmite) and $\text{NaCrSi}_2\text{O}_6$ are stable even under normal pressure, whereas the analogous compound $\text{NaAlSi}_2\text{O}_6$ is stable only under high pressures. The present study was aimed at investigating in more detail the conditions of forming and the stability of kosmochlor (ureyite) $\text{NaCrSi}_2\text{O}_6$.

EXPERIMENTAL PART

Several methods were combined in studying the conditions under which kosmochlor and eskolaite are formed. Following thermal exposure, the degree of conversion in the mixture of the starting substances was

established by a chemical method, while the reaction products were identified by X-ray diffraction and by optical microscopy. Use was also made of DTA, GTA and gas chromatography, as described in [1].

Starting substances

Silica was used in the form of SiO_2 sol of TOSIL trade mark, stabilized with ammonia and containing 29.27 wt.% or 30.27 wt.% SiO_2 . The following contents of impurities were established by AAS: 0.0022 wt.% Fe_2O_3 , 0.0005 wt.% Al_2O_3 and 0.0007 wt.% Na_2O . The sodium chromate and bichromate were of A.R. purity and prior to use were heated at 500 °C.

Preparation of the mixtures and their heat treatment

The homogeneous mixtures were prepared by blending the required amounts of silica sol and chromate solutions. The water was evaporated and the mixture dried at 140 °C. The powder was compacted into pellets 10 mm in diameter, 2 mm in thickness and on the average 0.3 g in weight. The pellets were first heated for 3 hours at 600 °C. The experiments proper were carried out in a Pt boat fitted with suspension eyelets of Pt wire, onto which the pellets were placed. This arrangement had the purpose to restrict as much as possible the contact with Pt, as the original experiments with powdered samples in a Pt crucible indicated a catalytic effect of platinum. An electric furnace with temperature control accurate to better than 5 °C was employed for the thermal exposure. The heat treatment was effected in air atmosphere.

Chemical determination of the conversion degree

The course of the reaction was followed quantitatively by photometric determination of unreacted chromium. The chromate-silica mixtures prepared and heat treated as described above were powdered to a

particle size of less than 0.09 mm. The soluble chromate, i.e. that which has not been converted into an insoluble product, was then dissolved by leaching the powder for 24 hours in HCl solution of $pH = 2$. The subsequent photometric determination of Cr in the solution made use of the yellow colour of chromate ions whose maximum adsorption occurs at a wavelength of 390 nm [4]. The result allows the conversion degree expressed as the proportion of reacted chromate to be calculated. The method by which the conversion degree would be determined by loss in weight was found to be unviable, probably due to rapid hydration of the residual chromate after thermal exposure and due to uncontrollable vaporization of chromium oxides during reduction of arising CrO_3 to Cr_2O_3 . Existence of the vaporization was indicated by green deposits on the suspension and on inner parts of the furnace.

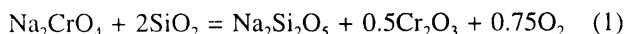
Structural analysis

The samples subjected to X-ray analysis were examined on the XRD 3000P apparatus by Seifert (FRG) including a diffractometer with Bragg-Bretan's arrangement. The measurement was effected at a continuous shift of 0.02° (2 θ)/s, the ratio of current and voltage input to the X-ray tube was 35 mA/35 kV. CoK α radiation and graphite monochromator were used. The interplanar distance values established were compared with the PDF 2 database [2].

The products obtained were also evaluated by optical microscopy. According to available data, kosmochlor, in contrast to eskolaite, exhibits very distinct pleochroism and a different structure of crystals. Kosmochlor is a monoclinic, optically negative mineral with characteristically emerald-green crystals of glassy lustre, up to 0.5 mm in size. Eskolaite is trigonal, with columnar crystals up to 1 cm in length, and tabular to base. They are dark green to black in colour and have a high gloss [5].

RESULTS AND DISCUSSION

The results of determining the conversion degree in the mixture $Na_2CrO_4 + 2SiO_2$ are plotted in figure 1. The plot shows that over the temperature range of 950 to 1050 $^\circ C$, a two-hour exposure resulted in a conversion of about 66 %, and that this value was not changed even by four-fold extension of this time of exposure. On the other hand, after thermal exposure at 1100 and 1150 $^\circ C$ the conversion degree increased to values close to 100 %, in the sense of the originally assumed reaction



At the lower temperatures the reaction will thus stop at two thirds of complete conversion degree, which indicates that the reaction proceeds in two stages according to the equations given below, of which the

former concerns the lower temperatures and the latter temperatures higher than 1050 $^\circ C$:

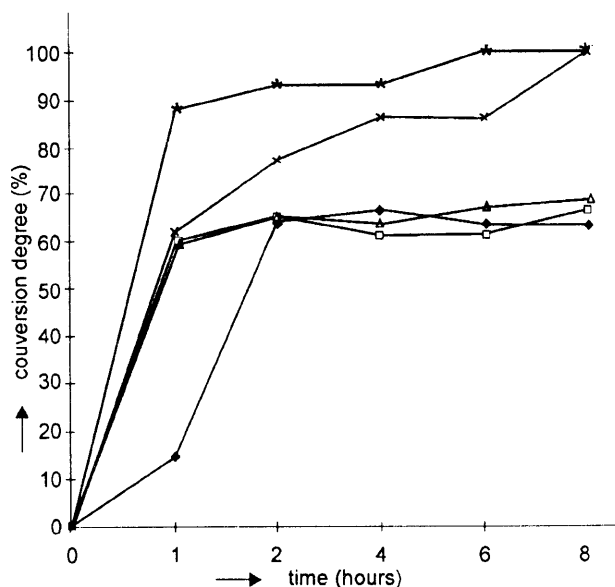
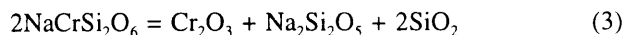
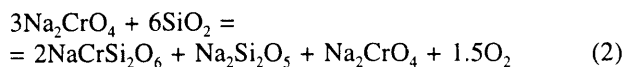


Figure 1. Conversion degree vs. temperature and time for the mixture $Na_2CrO_4 + 2SiO_2$.

◆ - 950 $^\circ C$, □ - 1000 $^\circ C$, Δ - 1050 $^\circ C$, × - 1100 $^\circ C$, * - 1150 $^\circ C$

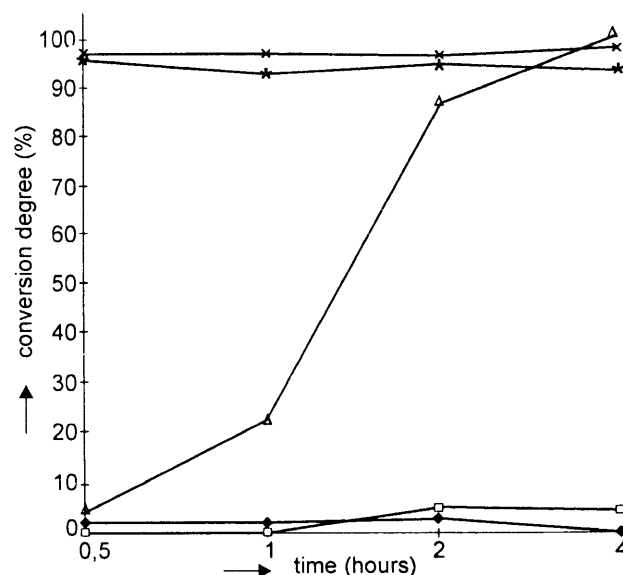
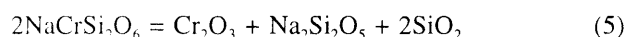


Figure 2. Conversion degree vs. temperature and time for the mixture $Na_2CrO_4 + 3SiO_2$.

◆ - 850 $^\circ C$, □ - 900 $^\circ C$, Δ - 950 $^\circ C$, × - 1000 $^\circ C$, * - 1050 $^\circ C$

According to this concept, unreacted chromate from reaction (2) successively reacts with SiO_2 released by decomposition of kosmochlor according to reaction (3). This concept concerns the mixture in which the chromate to SiO_2 ratio is 1:2. The chromate is considered to be unstable at high temperatures and to melt incongruently. The arising sodium silicate (m.p. < 900 °C) melts and forms a glass on undercooling. Figure 2 presents the results of conversion degree determination by the method described above in a mixture of sodium chromate and SiO_2 at a 1:3 ratio, which corresponds to the stoichiometry of the following reactions:



In this case all of the oxygen should be liberated by reaction (4) and the decomposition (5) no longer includes any release of oxygen. Figure 2 shows that no reaction involving reduction of the chromate takes place up to 900 °C. However, unlike the case of the mixture with a 1:2 ratio, the reaction proceeds to complete conversion within several hours already at 950 °C, and at 1000 °C the reaction is so fast that its onset cannot be detected. The mixture with the 1:3 ratio of starting substances thus reacts faster and a complete conversion is attained at a lower temperature than with the 1:2 mixture.

To verify the assumptions expressed by equations 2 through 5, the amount of oxygen liberated from the mixture was again determined by the gas chromatographic method, already employed in [1]. The results are plotted in the diagrams in figure 3 and are clearly indicative of a two-stage liberation of oxygen from the 1:2 mixture and of a single-stage one from the 1:3 mixture. In the latter case, the entire amount of oxygen is released over the temperature range of 900 to 1100 °C, that is at a lower temperature than in the former case, quite in agreement with the results shown in figures 1 and 2 and with equations 2 through 5. A more detailed analysis of the two-stage curve also implies that in the first stage, the reaction actually proceeds up to two thirds of complete conversion, which agrees to the analytical determinations.

In order to prove and supplement these conclusions, use was made of X-ray crystallographic and microscopic evaluation of the reaction products. The results for the 1:2 ratio of the starting substances are listed in table 1. After two hours of exposure to 950 °C and 1050 °C the reaction products comprise tridymite and kosmochlor, and the sample contains unreacted chromate hydrated by atmospheric humidity. Sodium silicate was not found, as at the given temperatures it melts and forms a glass on cooling. The presence of tridymite can be readily explained: it is produced by crystallization of the melt or of the amorphous unreacted SiO_2 . Chromic oxide in the form of eskolaite already begins to appear at 1050 °C as a result of an overlap of the two reaction stages

(reactions 2 and 3). At 1100 °C, the presence of eskolaite is already distinct and there are only small amounts of residual chromate. The appearance of kosmochlor and eskolaite crystals is illustrated by the optical micrographs in figures 4 through 7. All of the micrographs are of crystals obtained from mixtures with a 1:2 ratio of the starting substances.

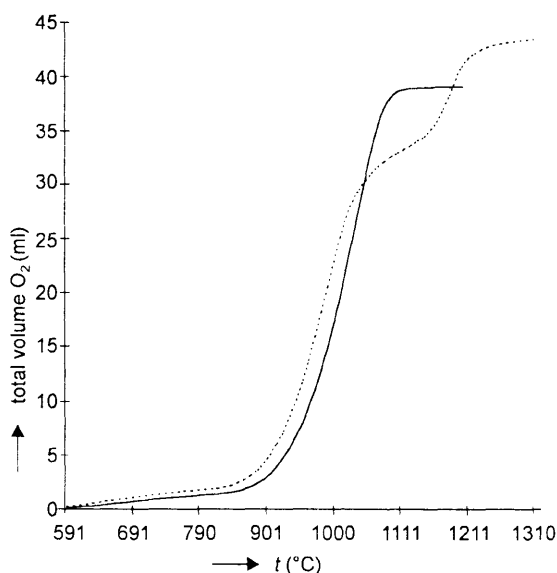


Figure 3. The amount of O_2 released from the mixture of sodium chromate with SiO_2 at the 1:2 and 1:3 ratios, as recorded by the gas chromatograph.

..... - $\text{Na}_2\text{CrO}_4 + 2\text{SiO}_2$, ——— - $\text{Na}_2\text{CrO}_4 + 3\text{SiO}_2$

Table 1. X-ray and microscopic analyses of products in the mixture of sodium chromate with SiO_2 (1:2).

temperature/time	X-ray diffraction and microscopy
950°C/2 hours	tridymite kosmochlor hydrated chromate
1050°C/ 2 hours	tridymite kosmochlor hydrated chromate weak lines of eskolaite
1100°C/ 2 hours	small amount of chromate small amount of kosmochlor eskolaite

Additional experiments were concerned with studying the conditions of stability and decomposition of kosmochlor. The kosmochlor was prepared from a mixture of sodium dichromate and SiO_2 sol by the assumed reaction

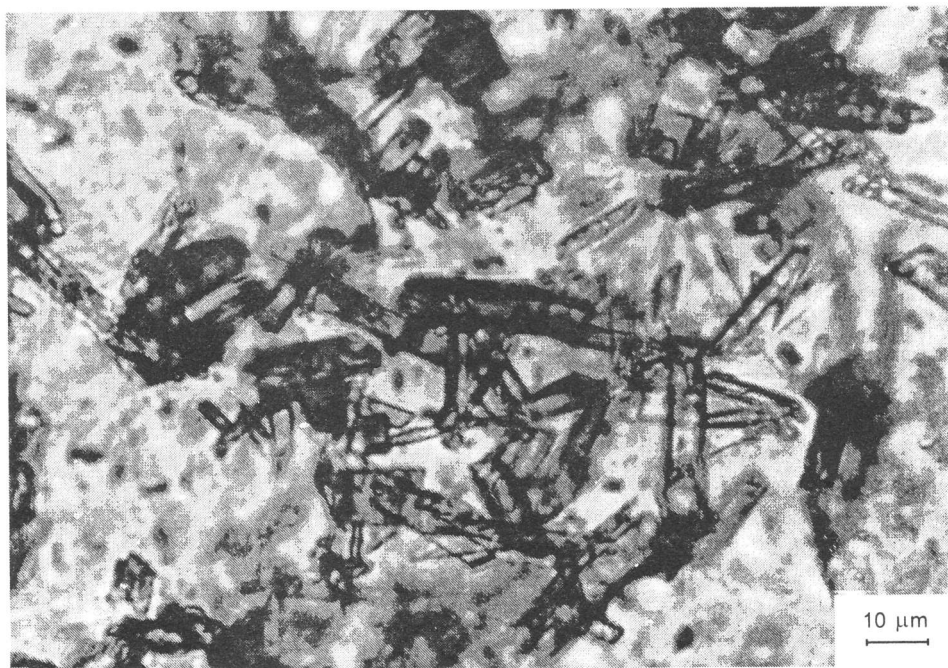


Figure 4. Columnar crystals of kosmochlor, $t = 950\text{ }^{\circ}\text{C}$, $\tau = 2\text{ hours}$.

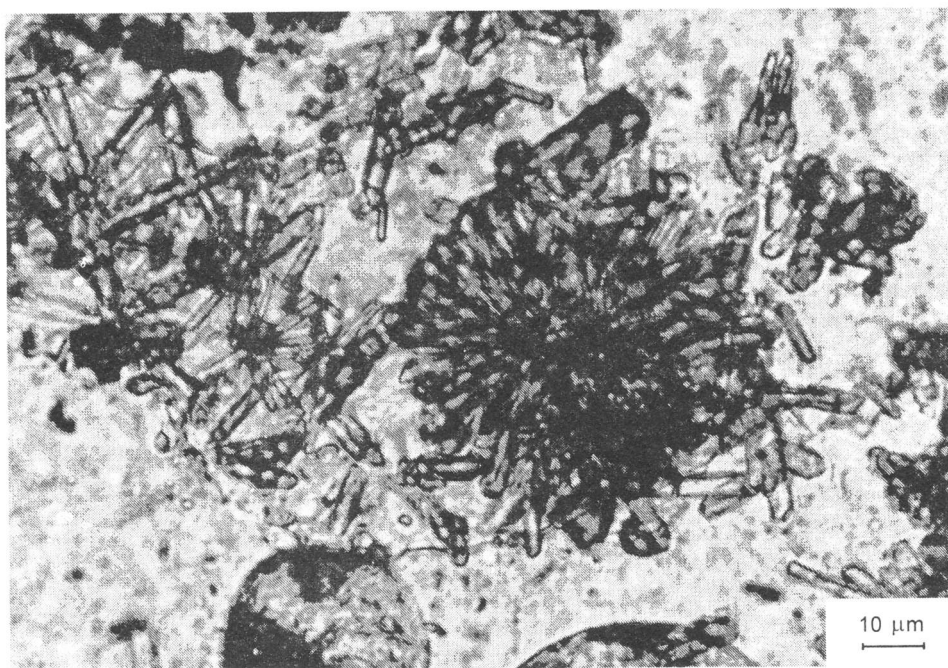


Figure 5. Crystals of kosmochlor in vitreous phase, to the right in a dendrite cluster, $t = 1050\text{ }^{\circ}\text{C}$, $\tau = 2\text{ hours}$.

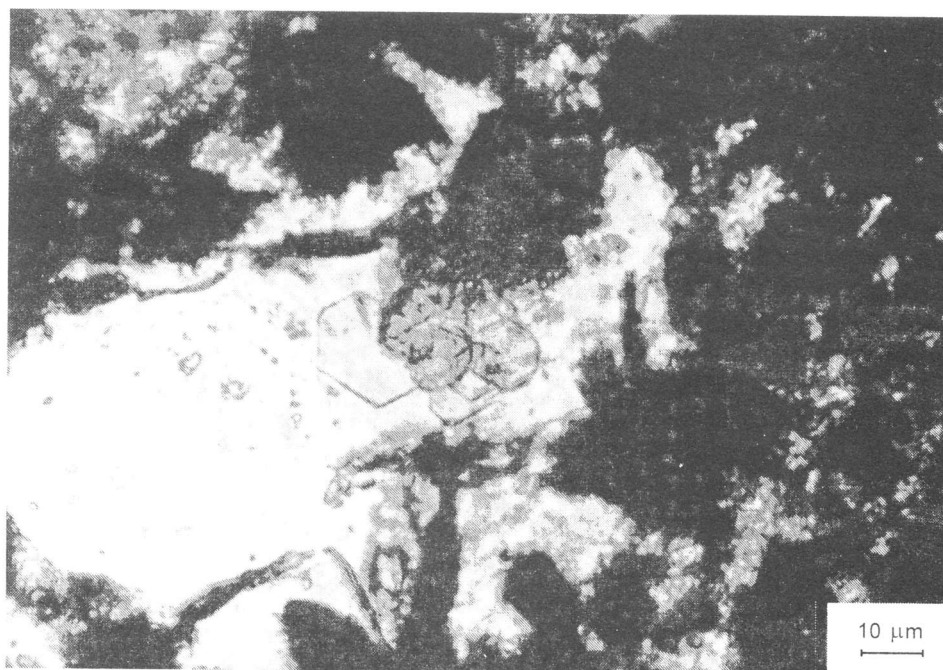


Figure 6. Hexagonal platelets of eskolaite, $t = 1100\text{ }^{\circ}\text{C}$, $\tau = 2\text{ hours}$.

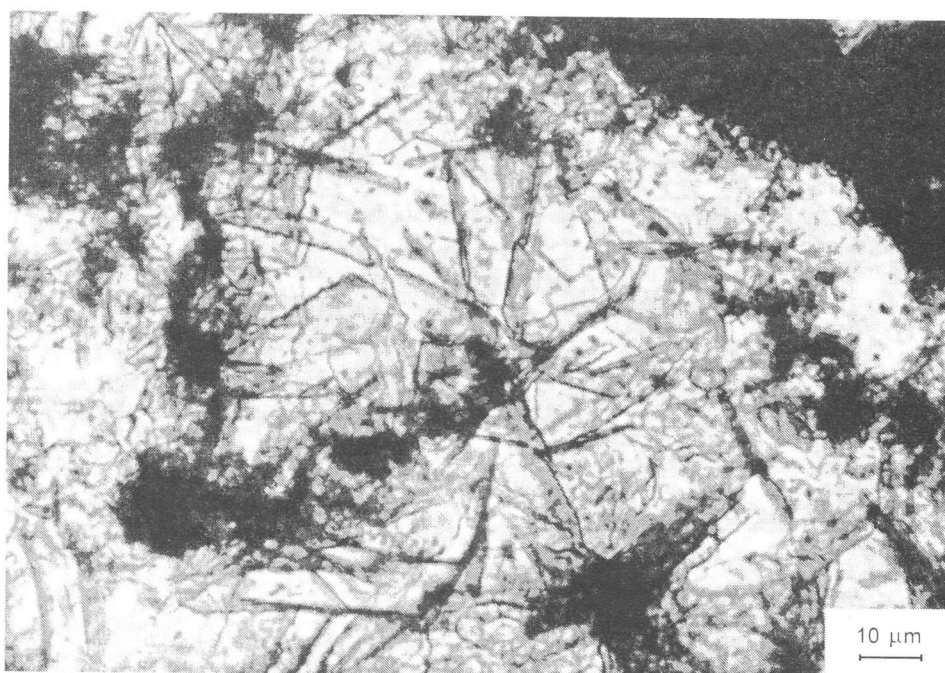
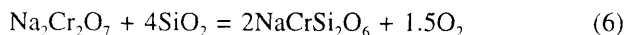
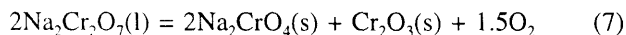


Figure 7. Cluster of corroded eskolaite crystals, $t = 1150\text{ }^{\circ}\text{C}$, $\tau = 2\text{ hours}$.



Sodium dichromate melts at 357 °C and decomposes above 400 °C [6]:



A DTA record of the dichromate employed revealed a distinct melting point at 364 °C but the DTA curve did not indicate the decomposition because this takes place over a wide temperature range. The DTA of a mixture with SiO_2 showed, apart from the melting point of dichromate, a wide but distinct endothermal effect with a minimum at 1045 °C, obviously pertaining to the formation of kosmochlor. The course of the reaction is better indicated by the GTA curve shown in figure 8. According to this curve, about one half of the oxygen is liberated by gradual dichromate decomposition up to 800 °C and the other half over the range of 1000 to 1130 °C. It may therefore be assumed that the decomposition of chromate to equation (7) is followed by reaction:

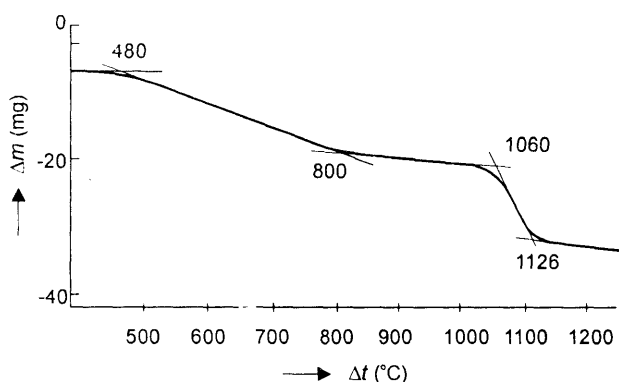
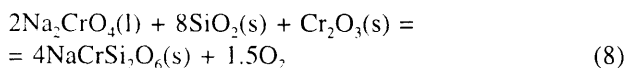


Figure 8. GTA record for the system $\text{Na}_2\text{Cr}_2\text{O}_7 + 4\text{SiO}_2$.

The formation of kosmochlor was again proved by X-ray analysis and optical microscopy. The results are summarized in table 2. Following thermal exposure at 1000 and 1040 °C for 2 and 4 hours, kosmochlor with a small amount of eskolaite was established as the dominant phase by X-ray analysis. Only kosmochlor was determined by microscopy after both 2- and 4-hour exposure. Kosmochlor is thus stable at the given temperatures. The small amount of eskolaite obviously stems from chromic oxide in the incompletely reacted mixture. No kosmo-chlor was found in the product after the 1100 °C exposure. The weak lines of cristobalite in

the X-ray patterns, which tend to disappear completely after some time, can also be ascribed to incomplete reacting of the mixture.

Table 2. X-ray and microscopic analyses of products obtained from the mixture of sodium bichromate and SiO_2 (1:4).

temperature/time	X-ray diffraction and microscopy
1000 °C/2 hours	kosmochlor weak lines of eskolaite
1000 °C/4 hours	kosmochlor weak lines of eskolaite
1040 °C/2 hours	kosmochlor weak lines of eskolaite
1040 °C/4 hours	kosmochlor weak lines of eskolaite
1100 °C/2 hours	prevailing eskolaite weak lines of cristobalite
1100°C/4 hours	eskolaite
1150°C/15 minutes	eskolaite

CONCLUSION

In mixtures of chromate and dichromate with SiO_2 , thermal exposure over the temperature range of 950 to 1050 °C yields as reaction product sodium chromium silicate (kosmochlor, ureyite) having the composition $\text{NaCrSi}_2\text{O}_6$. In non-stoichiometric mixtures containing excess chromate the reaction proceeds in two stages: The respective amount of kosmochlor formed at the lower temperature is decomposed at the higher temperature into the final product, in which Cr_2O_3 is stable. Kosmochlor alone can be prepared from the stoichiometric mixture $\text{Na}_2\text{Cr}_2\text{O}_7 + 4\text{SiO}_2$. In the systems being studied the compound in question begins to decompose at 1050 - 1100 °C, forming a melt and thus exhibiting the features of incongruent melting.

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VYSOKOTEPLOTNÍ REAKCE CHROMANU SODNÉHO S OXIDEM KŘEMIČITÝM

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Reakce mezi chromanem sodným a oxidem křemičitým byla sledována s cílem upřesnit podmínky vzniku a stability sloučeniny $\text{NaCrSi}_2\text{O}_6$ zvané kosmochlor.

Reakční směsi byly sestavovány ze solu oxidu křemičitého a vodného roztoku chromanu sodného. Po vysušení a přezhánění na 600 °C byly vzorky exponovány při různých teplotách a stupeň přeměny stanoven chemickým rozbořem. Identifikace produktů byla provedena rtg difrakcí a optickou mikroskopií, dále byly použity metody termické analýzy a plynové chromatografie.

Ve směsích chromanu a dichromanu sodného s SiO_2 se tvoří reakční produkt křemičitan sodno-chromitý (sodium chromium silicate - kosmochlor, ureyit) o složení $\text{NaCrSi}_2\text{O}_6$, a to v rozmezí teplot 950-1050 °C. V nestechiometrických směsích s přebytkem chromanu probíhá reakce dvoustupňově: za nižší teploty vznikne příslušné množství kosmochloru, který se při vyšší teplotě rozloží na konečný produkt, v němž je stabilní Cr_2O_3 . Samotný kosmochlor je možno připravit ze stechiometrické směsi $\text{Na}_2\text{Cr}_2\text{O}_7 + 4\text{SiO}_2$. Ve studovaných systémech se tato sloučenina začíná rozkládat při 1050 - 1100 °C za vzniku taveniny a jeví tedy znaky inkongruentního tání.