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Crystallization of triplet alkalies (Li, K, Na)-containing fluorrichterite glasses

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Abstract

Crystallization characteristics of glasses based on fluoramphibole containing three alkalies were investigated. The thermal behaviour of the glass samples was studied using DTA and their heat-treated samples were characterized by XRD and SEM. Fluorophlogopite, tainiolite, fluorrichterite, roedderite, enstatite and cristobalite phases were developed in the heat-treated glasses. The high Li-containing sample shows modification of the crystalline phases and the phase transformation at each DTA exotherm. Dominance of fluorophlogopite or fluorrichterite was detected in high K- and Na-containing samples respectively with enstatite as well. Crystallization at high temperature lowered the cristobalite phase in the high alkali-content glasses, whereas all samples showed formation of roedderite and enstatite on long duration heat-treatments. The microstructure of the glass–ceramic samples tends to be fine in the case of equal triplet alkalies (Li, K, Na)- and Na-containing samples whereas it became coarse in the high K-content samples. However, it was nonhomogeneous because of dendritic growths in the high Li-content ones. The coefficient of thermal expansion of glasses showed moderate values of 76–89 × 10^{-7} °C^{-1} (20–300 °C). However, in the corresponding glass–ceramics, and with exception of the highest Li-content glass–ceramic (72–78 × 10^{-7} °C^{-1}), these were relatively high especially for samples of highest K- and Na-contents (83–119 × 10^{-7} °C^{-1}). The density of the glass–ceramic samples (2.821–2.641 gm/cm^3) decreased in the order GNKL > GN > GK > GL > Grich.

Keywords: D. Glass–ceramic; Phlogopite; Tainiolite; Richterite; Roedderite

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1. Introduction

Glass–ceramics based on fluoramphibole represent a very important class of materials of wide range of compositions that can crystallize easily from their melts. K-fluorrichterite is a member of the fluoramphibole class and it has good durability and high strength and it is used in the manufacture of computer hard disks [1]. The stiochiometric fluoramphibole formula is $A0_{-1}B_2Y_5T_8\ O_{22}\ (OH, F, Cl)_2$, where A is a vacancy usually occupied by Na or K, B-site is occupied by either Na, Li, Ca, Mn, Fe, or Mg while the Y-site is occupied by Mg, Fe, Mn, Al, Fe^{3+} or Ti, and T (or the tetrahedral-position) is occupied either by Si or by Al [2].

The B-site occupancy is a key feature in amphibole crystal chemistry, and is the base of amphibole classification and nomenclature [3]. The solid solution between (Fe, Mg, Mn) and Na amphiboles in B-site is restricted in natural samples [4], whereas recent work on metasomatic episyenites of the Pedriza Massif (Spain) showed nearly complete solid solution between Li and Na amphiboles in B-site both with A-filled and A-empty sites [5,6]. Syntheses were done along the ferri-clinoferro-holmquistite $Li_2Fe_2{}^{+2}Fe_3{}^{+2}Si_8O_{22}(OH)_2$-riebeckite Na_2Fe^{2+} $2Fe^{3+}$ $2Si_8O_{22}(OH)_2$ join, where the exchange between Li and Na in B-site was complete.

A glass–ceramic based on fluoramphibole was prepared from ingredient chemicals [1]. Substitution of Li or Ca for Na in K-fluorricterite indicated that the presence of one sodium atom per formula unit is necessary for fluorrichterite crystallization [7]. Substitution of K and Li for Na in Mg-fluorricterite enhanced the formation of fluormica and protoamphibole respectively [8,9]. In crystallization of fluorcanasite–fluorrichterite glasses, the results indicate that during the crystallization of glasses containing more than 50% nominal fluorrichterite, elemental redistribution takes place whereby single-chain silicates (Ca–Mg metasilicates possibly with alkali metasilicates in solid solution) together with fluorrichterite to such an

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Table 1
Chemical compositions of the glass batches.

Sample	Stoichiometric fluorrichterite formula	Batch composition (wt%)						
		SiO_2	MgO	CaO	MgN_2	Na_2O	K_2O	Li_2O
Grich	$Na_2CaMg_5Si_8O_{22}F_2$[a]	58.46	19.61	6.82	7.58	7.54	–	–
GNKL	$Na_{0.65}K_{0.65}Li_{0.65}CaMg_5Si_8O_{22}F_2$	58.57	19.64	6.83	7.59	2.46	3.73	1.18
GK	$Na_{0.5}K_{2.0}Li_{0.5}Ca_{0.5}Mg_5Si_8O_{22}F_2$	56.59	18.98	3.30	7.34	1.82	11.08	0.88
GN	$Na_{2.0}K_{0.5}Li_{0.5}Ca_{0.5}Mg_5Si_8O_{22}F_2$	58.25	19.54	3.40	7.55	7.15	2.85	0.91
GL	$Na_{0.5}K_{0.5}Li_{2.0}Ca_{0.5}Mg_5Si_8O_{22}F_2$	60.00	20.12	3.50	7.78	1.93	2.94	3.73

[a] Stoichiometric fluorrichterite.

extent that fluorcanasite does not crystallize even in the more fully crystallized samples [10].

The present work deals with the crystallization characteristics of the stoichiometric fluorrichterite glass containing three different alkalies. The thermal behaviour and crystallization mechanism as well as some other properties were studied.

2. Experimental and materials

The glass batch compositions depend on the stoichiometric formulae of the fluorrichterite ($NaNaCaMg_5Si_8O_{22}F_2$). Mixtures corresponding to nominal compositions having site A either vacant or filled by Na substitutes and B-site of the stoichiometric fluorrichterite with K and Li were calculated, weighed and well mixed (Table 1). All compositions were prepared from ingredient chemicals. Calcium, magnesium, sodium, potassium or sodium was added as carbonates. Silica and fluorine were added as quartz sand and MgF_2 respectively. The glasses were produced by melting in a covered platinum crucible at 1350–1450 °C temperature range and annealing at 450 °C.

The thermal behaviour of each glass was determined using differential thermal analysis (DTA) technique. The DTA scans were carried out using a computerized system (Model DTA-7/Unix system, Perkin-Elmer) in a dynamic pure nitrogen atmosphere (flow rate of $50\ cm^3/min$). The heat-treatments were carried out according to the DTA results, i.e. at the endothermic and exothermic temperatures, or in the single-stage regime. The crystallized samples were identified by X-ray diffraction analysis using Cu-tube diffractometer (Philips, PW1390).

Different samples of fresh fractured surfaces were chemically etched using a 10% HF for 15 s. The etched samples were washed carefully with distilled water and gold layers of 5-μm thickness were sputtered over the polished surface. The microstructure of the coated samples was analyzed via SEM: Jeol-840A Electron Probe Microanalyzer operating at 20 kV. A mini scanning electron microscope (SEM-Jeol T-20) was used, on the freshly heat-treated specimen etched by $1\%HF + 1\%HNO_3$, to investigate the microstructures.

Coefficient of thermal expansion CTE was measured for glass and glass–ceramic samples using Linseis L74/1250 dilatometer. The densities of glass–ceramic samples were determined at room temperature by the Archimedes method using xylene as the fluid.

3. Results and discussions

3.1. DTA and XRD analysis

The DTA thermograms of the present glasses depict the effect of both the alkali variety as well as its contents on the crystallization behaviour (Fig. 1). The softening temperatures (endotherms) as well as the main crystallization temperatures (exotherms) decrease in the direction of the highest alkali contents in the samples containing dissimilar triple alkali, i.e. Li (GL) < Na (GN) < K (Gk) < LiNaK (GNKL) < only Na (Grich). The endothermic peak temperatures were in the 635–517 °C range, whereas the Grich base glass has the highest value and the GL glass, of the highest lithium ratio, has the lowest value (Fig. 1).

The exothermic peak temperatures range was 711–813 °C. When comparing peak characteristics, it must be noticed that the peak height decreased from the Grich base fluorrichterite to the GL glass of the highest Li content. However, increases of any alkali content in the glass enhance the crystallization, which is indicated by the increase of the exothermic peak

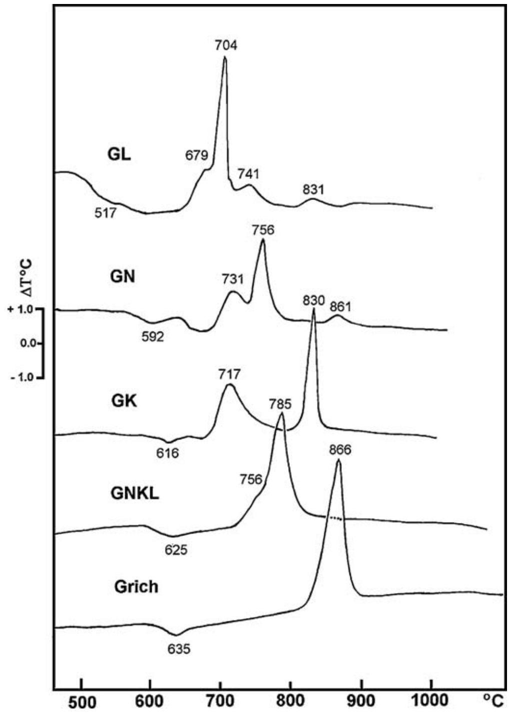

Fig. 1. DTA curves of the investigated glasses.

intensity. While the Grich base glass has only one exothermic peak at 865 °C, the GL glass has four peaks at 679, 704 (main), 741 and 831 °C.

Crystallization of the stoichiometric composition Grich at 750 °C shows amorphousity in the XRD pattern (Fig. 2). However, roedderite, fluorrichterite, and cristobalite were developed at higher temperatures (635 °C/2 h + 866 °C/2 h or 950 °C/10 h). In case of glass containing equal alkalies GNKL, fluorophlogopite and enstatite are developed on double and multistage heat-treatment (probably with some cristobalite at 750 °C/2 h). At higher temperatures, 950 °C for 10 h, roedderite and fluorrichterite were formed (Fig. 3).

Crystallization of the glasses containing a high concentration of one of the three alkalies, depends on the kind of the alkali. In the high K-containing sample, GK, fluorophlogopite became the dominant phase on the entire heat-treatment schedule with some enstatite. In high Na-containing sample, GN, fluorrichterite was the main phase with enstatite at low temperatures and with roedderite at higher temperature 950 °C for 10 h (Fig. 3). For the high Li-content sample, GL, formation of tainiolite and fluorrichterite took place in addition to enstatite and cristobalite at lower temperatures. However, at higher temperatures, roedderite appeared with the disappearance of cristobalite. Generally, in comparison of the DTA history, the GL glass modified the formed phases and phase transformation processes (Table 2 compares the data of GL, GN and GK).

Generally, the heat-treatment parameters of triplet alkalies containing glass samples, as well as their content, control greatly the developed phases. Li^+, Na^+ and K^+ have 0.23 Å, 0.19 Å and 0.13 Å field strengths respectively [11]. From the literature, the higher the field strength elements the easier the tendency of such elements to form crystalline phases. Therefore, Li^+ has a powerful effect on the crystallization tendency. Moreover, the lower temperature of melting of Li_2O as well as the easier mobility of Li ions during heat-treatment of glasses facilitate the crystallinity, in the sample of highest Li content. In addition, the presence of such percentages provides Li^+ ions to establish tainiolite formation that may be incorporated in the fluorrichterite structure.

Crystallization of fluorrichterite follows the presence of Na ions and it becomes dominant in the sample of the highest Na content. However, the highest percentage of K^+ hinders the crystallization of fluorrichterite and enhances the formation of fluormica, i.e. fluorophlogopite. In case of highest Li contents, both fluorrichterite and fluormica, i.e. tainiolite, are developed.

The pre-mentioned results show that, in fluosilicate glass-ceramics, K^+ is preferably accommodated in a layer structure [12]. Therefore, in high K-containing glass–ceramics a sheet structure fluormica was developed. In high Na- or Li-containing samples, the amphibole synthesis was sluggish [13]. Therefore, the crystallization of fluoramphibole followed the reaction of the early crystalline phases, fluormica and pyroxene, with residual glass [14–16]. Roedderite developed as the decomposition product of fluoramphibole [13].

The following equations may represent the transformation mechanism in GK, GN and GL glasses subjected to the heat-treatment (H.T.) process:

1. High K-containing glass:

$$\begin{aligned} \text{GK glass} &\xrightarrow{621\,^\circ\text{C}/2\,\text{h}+711\,^\circ\text{C}/2\,\text{h}} \text{fluorophlogopite} + \text{residual glass} \\ &\xrightarrow{+830\,^\circ\text{C}/2\,\text{h}} \text{fluorophlogopite} + \text{enstatite} \end{aligned}$$

2. High Na-containing glass:

$$\begin{aligned} \text{GN glass} &\xrightarrow{592\,^\circ\text{C}/2\,\text{h}+713\,^\circ\text{C}/2\,\text{h}} \text{enstatite} + \text{fluorrichterite} + \text{residual glass} \\ &\xrightarrow{+756\,^\circ\text{C}/2\,\text{h}} \text{fluorrichterite} + \text{enstatite} \end{aligned}$$

3. High Li-containing glass:

$$\begin{aligned} \text{GL glass} &\xrightarrow{517\,^\circ\text{C}/2\,\text{h}+680\,^\circ\text{C}/2\,\text{h}} \text{tainiolite} + \text{residual glass} \\ &\xrightarrow{+704\,^\circ\text{C}/2\,\text{h}} \text{tainiolite} + \text{enstatite} + \text{residual glass} \\ &\xrightarrow{+740\,^\circ\text{C}/2\,\text{h}} \text{cristobalite} + \text{enstatite} + \text{tainiolite} + \text{fluorrichterite} + \text{residual glass} \\ &\xrightarrow{+813\,^\circ\text{C}/2\,\text{h}} \text{tainiolite} + \text{roedderite} + \text{fluorrichterite} \end{aligned}$$

3.2. Microstructure of glass–ceramics.

The SE micrographs of the present glasses heat-treated at 850 °C for 2 h are shown in Fig. 4. The microcrystalline structure of the Grich sample depicts homogenous very fine grain texture of roedderite, fluorrichterite and cristobalite phases. The microstructure becomes finer and compact in the case of equal alkalies- and high Na-containing samples wherein very small crystals of only roedderite and fluorrichterite are precipitated. Crystallization of fiber crystals of enstatite and fluorophlogopite in the case of high K-containing glass make the structure coarser. In the presence of high Li-containing sample, coarse grained dendritic crystals in nonhomogenous microstructure of enstatite, roedderite and fluorrichterite were obtained.

Generally the microstructure of glass–ceramics tends to be finer in case of equal alkalies and Na-containing samples whereas it becomes coarser in high K-containing samples.

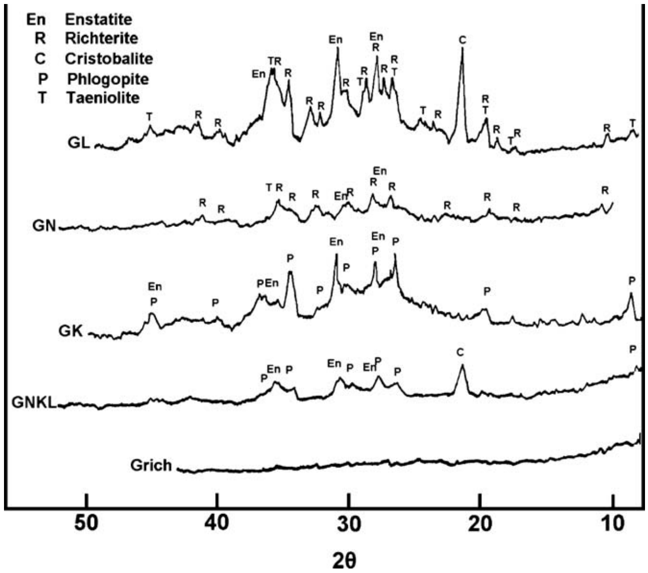

Fig. 2. X-ray diffraction patterns of the investigated glasses heat-treated at 750 °C/2 h.

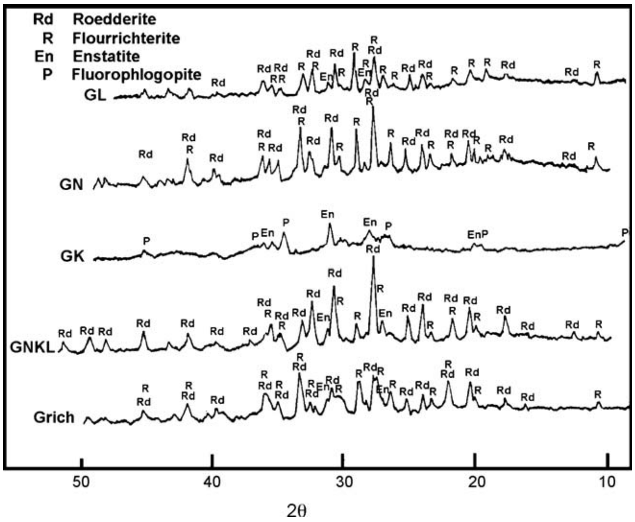

Fig. 3. X-ray diffraction patterns of the investigated glasses heat-treated at 950 °C/10 h.

However, it was nonhomogenous for dendritic growths in the case of high Li-containing samples.

3.3. Coefficient of thermal expansion and densities. The CTE results of the studied glasses show a maximum value of T_g (°C) for the base glass Grich (584 °C). This value decreased gradually from GNKL, GK, GN to a minimum of 535 °C in case of GL sample. The CTE of these glasses shows moderate values ($76–89 \times 10^{-7}$ °C^{-1}). However, such value was low for Grich base glass and for equal triplet alkalies containing glass but it was high for the sample containing high contents of Li, K and Na respectively (Table 3).

The CTE of glass–ceramic samples, in general, was higher than that of the corresponding glasses with the exception of

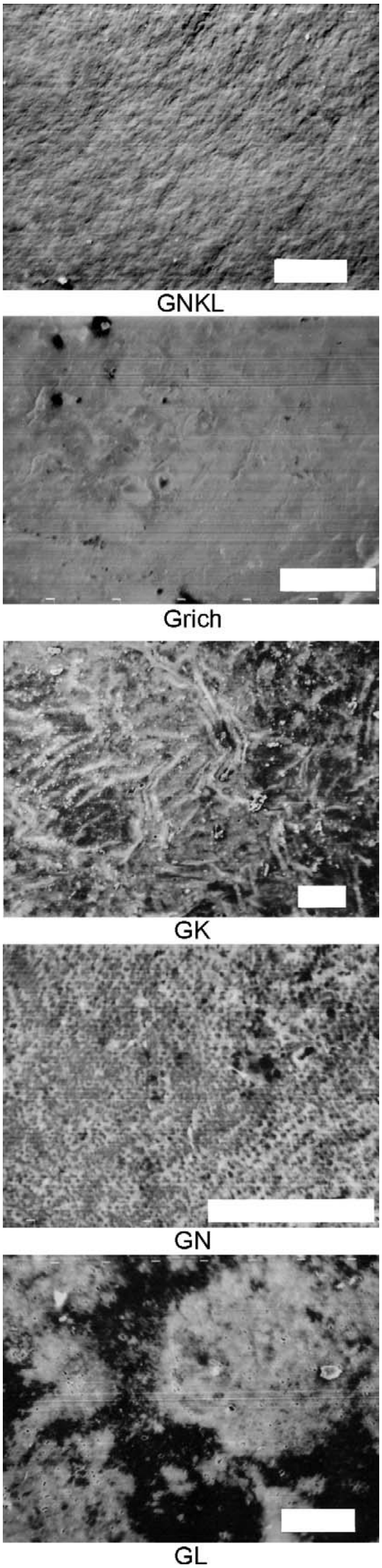

Fig. 4. SM micrographs of the investigated glasses heat-treated at 850 °C/2 h (bar = 30 μm).

Table 2
Characteristic of the heat-treated glasses.

Glass code	Heat-treatment parameter (°C/h)	Developed phases
Grich	635/2 + 866/2	Rich + Rd + Crist
	750/2	Amorphous
	950/10	Rd + Rich + En
GNKL	$a - 625/2 + 756/2$	Ph + En
	$b - a + 785/2$	Ph + En
	750/2	Crist + En + Ph
	950/10	Rd + Rich + En
GK	$a - 621/2 + 711/2$	Ph
	$b - a + 830/2$	Ph + En
	750/2	Ph + En
	950/10	En + Ph
GN	$a - 592/2 + 713/2$	En + Rich
	$b - a + 756/2$	Rich + En
	750/2	Rich + En
	950/10	Rd + Rich + En
GL	$a - 517/2 + 680/2$	Ta
	$b - a + 704/2$	Ta + En
	$c - b + 740/2$	Crist + En + Tain + Rich
	$d - c + 813/2$	Tain + Rd + Rich
	750/2	Crist + En + Tain + Rich
	950/10	Rd + Rich + En

Ph: fluorophlogopite, Rich: fluorrichterite, Rd: roedderite, Ta: tainiolite, En: enstatite, Crist: cristobalite.

Table 3
Thermal expansion characteristics of the glasses.

Glass code	Thermal behaviour		CTE, $\alpha \times 10^{-7}\,^{\circ}C^{-1}$
	T_g (°C)	T_s (°C)	20–300 °C
GNKL	566	590	76
Grich	584	622	77
GK	547	591	85
GN	538	578	89
GL	535	567	81

Table 4
Thermal expansion coefficients α of glass-ceramics.

Sample code	CTE of glass–ceramic $\alpha \times 10^{-7}\,^{\circ}C^{-1}$			Density (g/cm^3)	Crystalline phases
	20–300 °C	20–500 °C	20–700 °C		
GNKL	83	86	91	2.821	Ph + En
Grich				2.641	Rich + Rd + Crist
GN	101	106	119	2.781	Rich + En
GK	101	103	113	2.752	Ph + En
GL	72	73	78	2.745	Tain + Rd + Rich

The density of the samples heat-treated at 850 °C/2 h (Table 4) shows a decrease in such values in the order GNKL (2.821 g/cm^3) > GN > GK > GL > Grich (2.641 g/cm^3). These changes in densities may be due to increase the coarsening and decrease of the compactness in the microstructure.

the GL sample which has the lowest value (Table 4). These values increased slightly for samples containing triplet alkalis (i.e. in high K- and Na-containing glass–ceramics). It was noticed that there are small changes in the slop of the curve of GN and GK. This change is a shift to higher temperature in GK. Although the previous work gave the CTE values of the developed phase, like for fluorophlogopite 6.4–7.1 × $10^{-6}\,^{\circ}C^{-1}$, enstatite 7.5–10.0 × 10–6 $^{\circ}C^{-1}$ and fluorrichterite with cristobalite 115 × $10^{-6}\,^{\circ}C^{-1}$ [1], nevertheless, in this work, the residual glass contains an alkali which plays an important role in increasing the CTE values. However, glass–ceramic samples containing high fluorrichterite ratio has the highest CTE value.

4. Conclusion

Crystallization of stoichiometric fluorrichterite NaNaCaMg$_5$Si$_8$O$_{22}$F$_2$ glasses containing high concentration of specified alkali, from the triplet alkalies (Na, K, Li) CaMg$_5$Si$_8$O$_{22}$F$_2$, depends on the kind of the alkali. Fluorrichterite becomes dominant in the sample of the highest Na content while K$^+$ in highest percent hinders the crystallization of fluorrichterite and enhances the formation of fluormica, i.e. fluorophlogopite. In case of highest Li contents, both fluorrichterite and fluormica, i.e. tainiolite, are developed. The microstructure of glass–ceramics tends to be finer in case of equal alkalies- and Na-containing samples whereas it became coarser in high K-containing samples. However, it was nonhomogenous of dendritic growths in high Li-containing ones. The CTE of the fluorrichterite glasses shows moderate values (76–89 × $10^{-7}\,^{\circ}C^{-1}$). However, in the corresponding glass–ceramic samples, with exception of highest Li-containing sample (has 72–78 × $10^{-7}\,^{\circ}C^{-1}$ value), such CTE values were relatively high (83–119 × $10^{-7}\,^{\circ}C^{-1}$). The densities of the samples show a decrease of values from GNKL (2.821 g/cm^3) > GN > GK > GL > Grich (2.641 g/cm^3).

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