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Preparation and characterization of barium containing refractory materials

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Abstract

Two grades of barium-containing refractory grains were processed from low and high purity materials by sintering methods after firing up to 1700°C. The first one was prepared from highly pure Al_2O_3 and $BaSO_4$, while the second one was prepared from raw Egyptian barite and Chinese bauxite. The densification parameters in terms of bulk density and apparent porosity were determined using the water displacement method. XRD was used for qualitative determination of phase composition, while SEM attached with an EDS unit was applied to study microstructure and microanalysis of the formed phases. The results reveal that grains processed from pure materials show BA_6 as a major phase with lower densification and open pores as compared with those prepared from commercial materials which exhibit higher densification and direct-bonded celsian/celsian and celsian/corundum phases with minor closed pores. The presence of higher amount of fluxing oxides, especially SiO_2 and Fe_2O_3 in the latter one has contributed in lowering its densification temperature and refractoriness as well as increasing its cold crushing strength. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Several barium compounds are interesting as starting materials for processing refractory and engineering ceramics, e.g. barium aluminates and titanates. According to the phase diagram of BaO–Al_2O_3 system [1], barium oxide (BaO), barium monoaluminate (BA: $BaO{\cdot}Al_2O_3$) and barium hexaaluminate (BA_6: $BaO{\cdot}6Al_2O_3$) are refractory materials having melting temperatures of about 1920, 1800 and 1900°C, respectively. Also, compositions with a BaO/Al_2O_3 molar ratio of 1:4.5 to 1:6.6 were selected either as binding materials for refractory castable or to make engineering ceramics [2–5]. Refractory BA_6 could be used as an alternative product to alumina–chromia refractories that have recently been found to be carcinogenic [6–7].

Different methods were used for the preparation of BA_6, among these were solid state, chemical and hydrothermal processes [8–12].

BA_6 as calcium and strontium hexaaluminates has the space group D^4_{6h}-hexagonal crystal system with two molecules per unit cell. Pressed and sintered BA_6 can produce mechanically strong components (MOR≅600 MPa). Due to the high temperature needed to produce these bodies, low-grade raw materials containing some impurities as a densification aid were used [13].

The objective of the present work is to study the processing of dense BA_6-bearing refractory grains using raw Egyptian barite and Chinese bauxite, as compared with those processed from chemically pure $BaSO_4$ and Al_2O_3. Densification parameters, mechanical properties and refractoriness of the grains fired up to 1700°C were followed in relation to their phase composition and microstructure.

2. Materials and methods

The raw materials used in processing of low grade barium hexaaluminate were Egyptian barite and Chinese calcined bauxite, while highly pure barium hexaaluminate was prepared using chemically pure $BaSO_4$ and Al_2O_3. The various raw materials were investigated for their mineralogical and chemical compositions using XRD Fig. 1 and wet chemical analysis Table 1,

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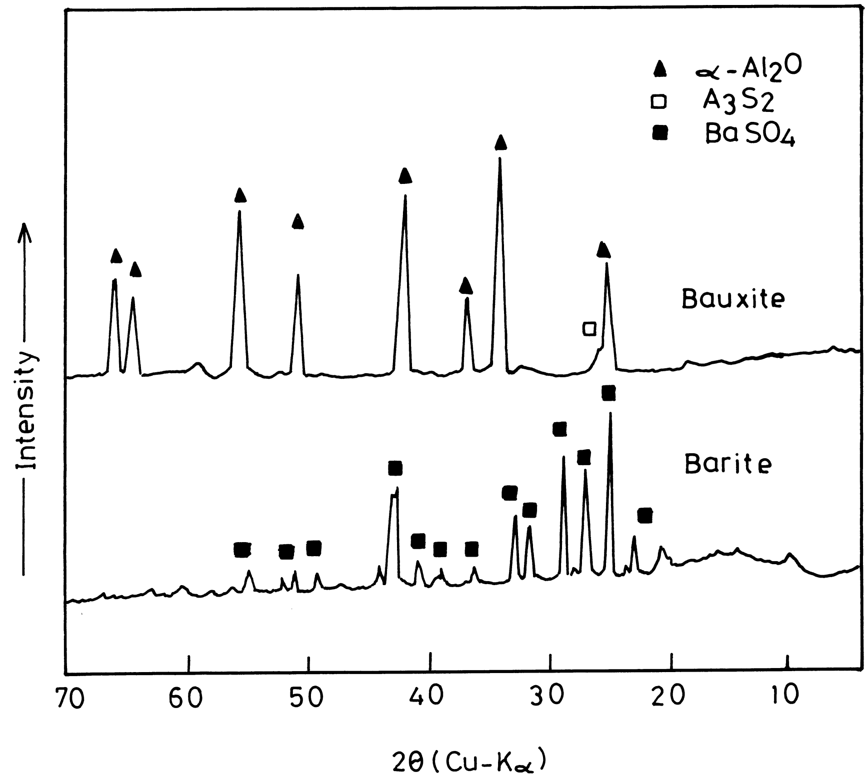


Fig. 1. XRD patterns of Egyptian barite and Chinese bauxite.

respectively. It appeared from Fig. 1 that calcined bauxite shows mainly Bragg's peaks of corundum (α-Al_2O_3) with only one line for mullite ($3Al_2O_3{\cdot}2SiO_2$), whereas barite is composed mainly of barite mineral ($BaSO_4$).

Concerning the chemical composition of bauxite, it contains 86.0% Al_2O_3 beside some SiO_2 (6.7%), TiO_2 (3.73%) and Fe_2O_3 (2.62%) in decreasing order. In addition, trace amounts of CaO, MgO and alkali oxides are detected. On the other hand, a sample of barite contains, on a calcined basis, 91.74% BaO, 5.67% SiO_2 and 2.30% total Al_2O_3, Fe_2O_3 and MgO.

Two mix compositions were prepared stoichiometrically from fine barite and calcined bauxite (M1) and from chemically pure $BaSO_4$ and Al_2O_3 (M2). The mixes were ground for 3 h until 200 μm fineness was achieved using a ball mill. The batches were uniaxially pressed under 100 N/mm^2 into 5×5×5 cm cubic samples and fired up to 1700°C in order to follow up the formation of BaO-bearing phases. Thereafter, the fired bodies were investigated for their phase composition, microstructure as well as physico–mechanical and refractory properties.

The densification parameters were followed by determining bulk density and apparent porosity adopting the water displacement method [14]. The phase composition was qualitatively determined using a Philips (PW 1710) Diffractometer. using Cu–K$_\alpha$ radiation. The microstructure was investigated using a Philips XL 30 scanning electron microscope attached to an EDS unit. The surfaces of dense samples were gradually polished using subsequent grades of SiC papers and diamond pastes. The polished surfaces were then cleaned under water by ultrasonic waves before coating under vacuum with a thin layer of gold (≈3 nm) for SEM investigation.

The mechanical properties in term of cold crushing strength (CCS) of the fired grains was carried out using a hydraulic machine of SEIDNER, Riedlinger, Germany, having a maximum loading capacity of 600 KN. The fusion temperature range (i.e. refractoriness) was determined using the cone fusion test [14].

Table 1
Chemical analysis data of calcined bauxite and barite raw materials

Oxides (wt.%)	Calcined bauxite	Egyptian barite
SiO_2	6.70	3.83
Al_2O_3	86.00	0.61
Fe_2O_3	2.62	0.53
BaO	–	62.00
CaO	–	0.42
MgO	–	–
TiO_2	3.73	–
NaO	–	–
K_2O	–	–
I.L.	–	32.42

3. Results and discussion

Fig. 2 shows the main peaks characterizing BA_6 in M1 at 1400°C, with some peaks related to unreacted Al_2O_3. The intensity of the latter peaks decreases by firing at 1550°C and almost completely disappeared at 1700°C at which all peaks characterizing BA_6 could be detected. This means that the reactions forming BA_6 are completed after firing up to 1700°C.

In M2 (Fig. 3), a small amount of BA_6 was detected at 1400°C, while the main peaks characterizing the refractory celsian (BAS_2) could be identified. In addition,

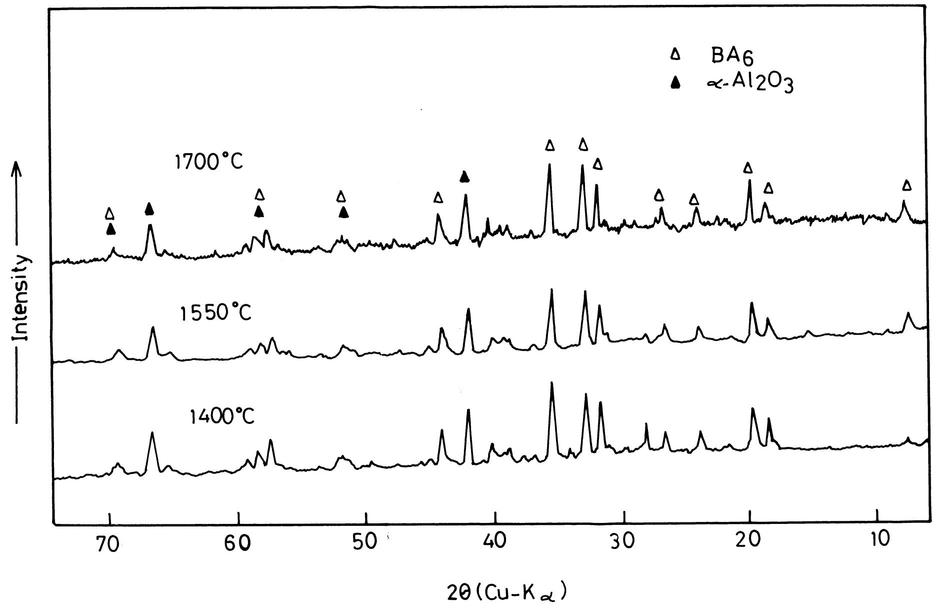


Fig. 2. XRD patterns of M1 grains after firing up to 1700°C.

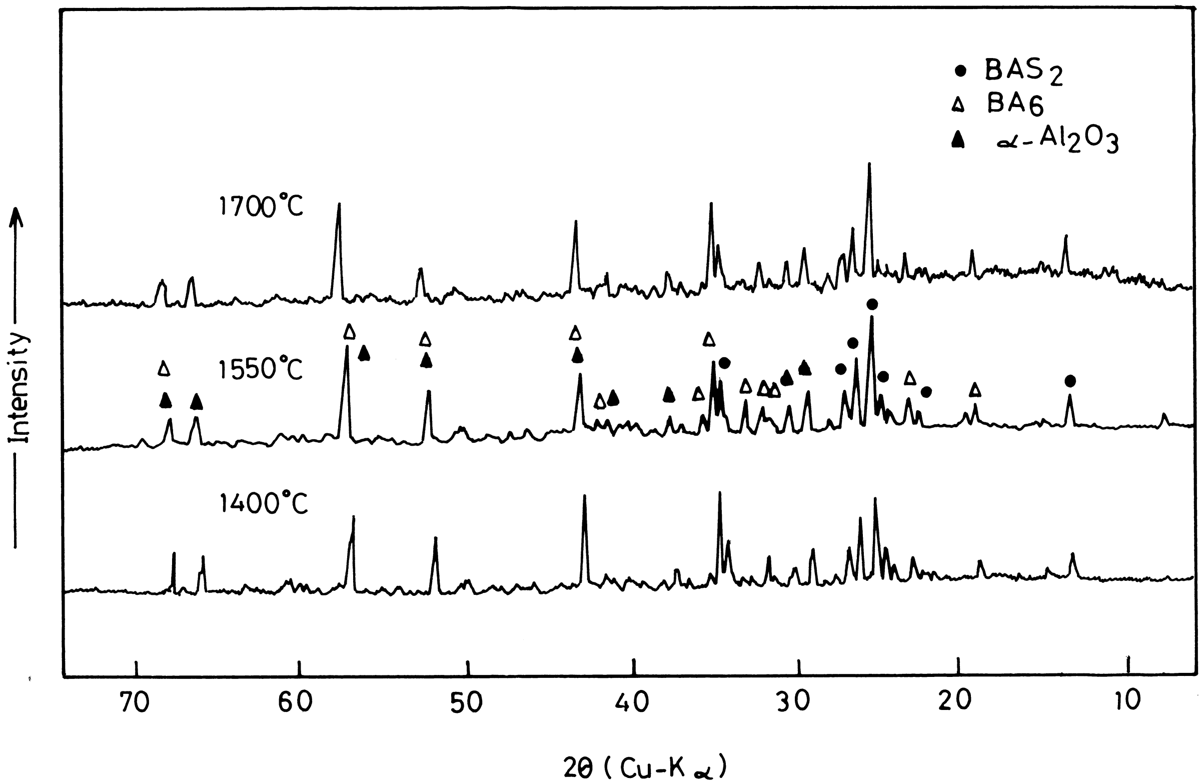


Fig. 3. XRD patterns of M2 grains after firing up to 1700°C.

some peaks relevant to residual Al_2O_3 were detected. By firing at 1500 and 1700°C no change in these patterns was observed. This means that the reactions were completed at a relatively lower temperature in M2 due to the presence of some impurities, especially SiO_2, that lead to the formation of a liquid phase beside celsian as a major phase.

Satish [15] concluded that di-hydrated barium chloride ($BaCl_2{\cdot}2H_2O$) additions to mixtures processed for the synthesis of BA_6 from $Al_2O_3+BaCO_3$ and $Al_2O_3+BaSO_4$ significantly accelerated the reaction. This effect may result from low-melting liquids which form due to the presence of chlorine Cl^- and sulphate SO_3^{3-} ions. Therefore BA_6 can be synthesized at lower temperatures when a mixture of $BaSO_4$ and $BaCl_2{\cdot}2H_2O$ is used, than when only $BaSO_4$ is used. Davies also concluded that aluminum–barium oxide precursor gels, with or without chromium (III), give a strong refractory product. The temperature required to obtain good grain bonding is reduced when chromium (III) is added [7].

The densification parameters such as bulk density and apparent porosity of the sintered M1 and M2 grains are shown in Fig. 4. From Fig. 4 M1 shows about 45%

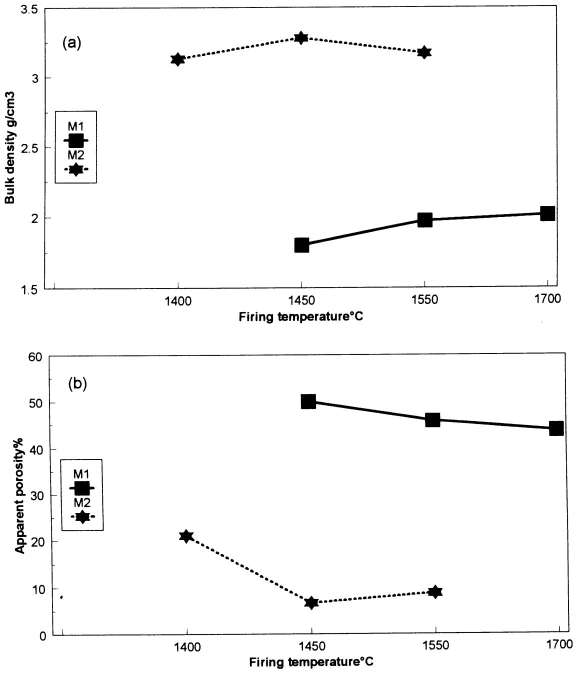
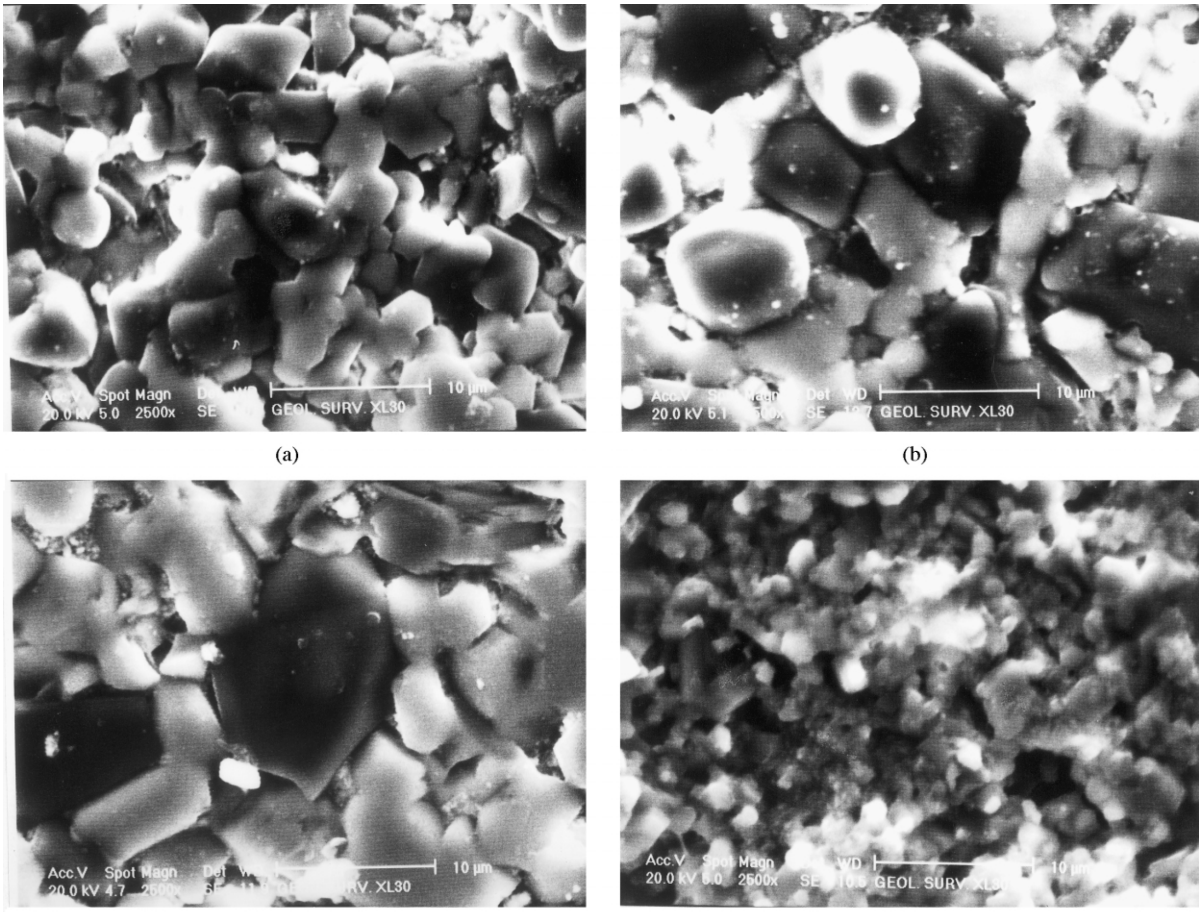


Fig. 4. Densification parameters of barium-bearing grains after firing up to 1700°C.



(a) (b)

(c) (d)

Fig. 5. SEM photomicrographs of M1 sample after firing at (a) 1400°C, (b) 1450°C, (c) 1550°C and M2 sample after firing at (d) 1700°C.

apparent porosity and ≈1.98 g/cm^3 bulk density after firing up to 1550°C. On rising the firing temperature up to 1700°C, the porosity is appreciably decreased to 43.7% with a relative increase in bulk density to 2.05 g/cm^3. In M2, the apparent porosity decreases sharply from 21.00 to 6.69%, whereas the bulk density rapidly increases from 3.13 to 3.28 g/cm^3 at 1400–1550°C. The presence of fluxing oxides in M2 leads to the development of a liquid phase which decreases the porosity and increases the density by raising the firing temperature, whereas M1 contains no fluxing oxides, so it needs higher temperature for sintering (> 1700°C) [7,15].

The phase arrangement, i.e. microstructure as well as microanalysis of each coexisting phase in the dense barium-containing grains after firing up to 1700°C, were revealed by SEM of their polished surfaces. The SEM photomicrographs obtained at two magnifications are shown in Fig. 5, whereas the quantitative microanalysis data are summarized in Table 2. It appeared that M1 grains contain rounded BA_6/BA_6 network with inter- and intra-granular pores having variable sizes. The microanalysis of plain BA_6 crystals (point Nos. 2 and 3) illustrates the solid solubility of a small amount of CaO and SiO_2 in its structure. Microanalysis of M1 (point No. 1) shows the BA_6 phase with a lower BaO/Al_2O_3 ratio, as well as some CaO and Fe_2O_3 in solid solution. On the other hand, the commercial barium-containing grains (M2) as shown in Fig. (5a–c) exhibit a higher degree of direct bonding between celsian/celsian and celsian/alumina phases. Both of the inter-and intra-granular pores of these grains are reduced as compared with those processed from pure material. By increasing the firing temperature from 1400 to 1550°C the degree of direct-bonding increases with discontinuous grain growth due to the solution precipitation mechanism [16,17]. The microanalysis data of M2 sample fired between 1400 and 1550°C confirm the development of celsian, besides free, α-Al_2O_3. The former phase contains some Fe_2O_3, K_2O and CaO in solid solution, whereas the latter phase includes only 0.5–3.2% Fe_2O_3. At 1400°C, α-Al_2O_3 exists together with nonstoichiometric celsian with excess alumina or excess BaO at the expense of its content of SiO_2.

Table 3 summarizes the cold crushing strength (CCS) and refractoriness of M1 and M2 samples after firing up to 1700°C.

It appeared that C.C.S. of M1 is still very low even after firing at 1700°C due to the higher porosity of the fired bodies which need a higher temperature than 1700°C for densification. These results confirm the data obtained for microstructure and densification parameters. Meanwhile, M2 grains give higher CCS values at all firing temperatures, with a maximum at 1450°C. This is due to the higher degree of densification obtained on firing at 1400–1550°C. The presence of some impurities leads to the formation of the celsian and silicate glassy phase, which contributes to the densification process and consequently increases the CCS. On raising the firing temperature, CCS increases from 90 to 135 MPa at 1450°C and then decreases to 100 MPa at 1550°C. This may be due to the grain growth of the developed phases after firing at 1550°C which leads to deterioration of the CCS.

Table 2
Point analysis of M1 and M2 refractory samples fired at different temperatures

	M1			M2								
	1700°C			1400°C			1450°C			1550°C		
Oxides	Point (1)	Point (2)	Point (3)	Point (1)	Point (2)	Point (3)	Point (1)	Point (2)	Point (3)	Point (1)	Point (2)	Point (3)
Al_2O_3	88.99	76.68	74.37	39.97	95.90	20.16	97.02	29.61	27.31	96.79	25.26	25.26
SiO_2	–	0.90	0.95	19.79	–	14.16	–	29.60	29.48	–	29.50	29.74
CaO	1.87	–	0.57	0.79	–	0.46	–	–	0.30	–	–	–
BaO	8.45	22.43	24.11	37.26	–	63.83	–	39.34	41.69	–	44.70	44.34
Fe_2O_3	0.69	–	–	2.36	4.10	1.39	2.98	1.06	0.87	3.21	0.74	0.65
K_2O	–	–	–	–	–	–	–	0.40	0.35	–	–	–

Table 3
Cold crushing strength (CCS) and refractoriness of barium-containing refractories after firing up to 1700°C

	M1[a]		M2[a]		
Properties	1550	1700	1400	1450	1550
CCS (MPa)	9	17	90	135	100
Refractoriness (°C)	> 1700		≈1700		

[a] Firing temperature (°C).

The development of liquid phase up to 1700°C in M2 is responsible for its partial fusion at 1700°C as compared with M1 which shows higher melting temperatures, i.e. refractoriness (>1700°C), as illustrated in Table 3. The higher refractoriness of M1 than M2 indicates the high refractory quality of the former material and it may exhibit a good refractoriness underload and creep resistance.

4. Conclusion

The results reveal that grains processed from pure materials show BA_6 as a major phase, with lower densification and open pores, compared to those prepared from commercial materials which exhibit higher densification and direct-bonded celsian/celsian and celsian/corundum phases with minor closed pores. The presence of a higher amount of fluxing oxides, especially SiO_2 and Fe_2O_3 in the latter case, has contributed in lowering its densification temperature and refractoriness as well as increasing its CCS. Consequently it decreases the refractory quality of these materials as compared with pure materials. The high refractory properties of pure materials fit the refractory industry requirement, whereas the commercial ones are not compatible with the refractory industry at high temperatures ($\geqslant$1700°C) or it can be used in non-severe conditions.

Generally it is recommended that BA_6-bearing materials are used as alternative products to alumina–chromia refractories that have recently been found to be carcinogenic. Also, they can be used as binding materials for refractory castable or to make engineering ceramics.

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