

Effect of the enucleating agent on Indialite-cristobalite Glass-Ceramics

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ABSTRACT

Silica sand, clay, magnesite and some laboratory reagent (LR) were used in synthesis of Indialite- cristobalite glass-ceramics. The characterization of prepared sample was carried out by means of diffraction thermal analysis (DTA), X-ray Diffraction (XRD), Scanning Electron Microscopy and Dilatometer (DIL). The DTA of $2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$ system were determined in the range of $800-1125^\circ\text{C}$ of nucleated and non nucleated samples. The effects of nucleating agents such as TiO_2 , LiF and $\text{TiO}_2+\text{Cr}_2\text{O}_3+\text{LiF}$ at different heat treatment temperature (800°C , 900°C , $1000^\circ\text{C}/8\text{hrs}$ each and $1100^\circ\text{C}/40\text{hrs}$) on crystallization and morphology were also studied. The XRD analysis results showed the hexagonal metastable form of cordierite or - cordierite (Indialite) as a major phase. Anorthite, enstatite, cristobalite and spinel phases were also recognized at higher temperatures. The heat treatment schedule showed effects on the crystallization of different phases, while role of time was not reflected in any crystallized samples. The variation in the crystal size and phases

INTRODUCTION

Cordierite ($2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$) glass-ceramics material has a wide range of uses and applications stemming from its important properties of low thermal expansion and dielectric constant coupled with high chemical and thermal stability. All these characteristics of glass-ceramics

depend upon phase composition, crystalline and amorphous ratio. These are indirectly controlled by batch composition, type of nucleating agent and heat treatment. Every phase has its own characteristics. Now days wide applications of glass- ceramics require different properties of materials. Indialite consists of the six-membered rings formed by five silicon and aluminum tetrahedral that share corners. Other aluminum tetrahedral and magnesium octahedral network connect the alternate six-membered (hexagonal) rings in such a manner that two structural cavities or channels per formula unit parallel to the c -axis are formed. Earlier, investigators reported osumilite and petalite, the two metastable phases during devitrification of glass of certain bulk composition at relatively low sub solidus temperatures (Schryrer & Schairer, 1961). Other related studies also showed wide range of crystallization in the composition of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system (Pinckney & Beall, 1997; Stooky, 1960; Zdaniewski, 1975 & 1978 ; Watanabe et al, 1994; Putinis et al, 1987 and Barry et al, 1973). Omer and Elshennawi 1971 confirmed the finding of Merwin (1918) of a stable form of cordierite now known to be hexagonal polymorph of $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_8$, indialite which crystallizes between 950°C and 1470°C from a glass of requisite composition. This phenomenon indicated that the formation of the α -cordierite is temperature dependent rather than time-dependent. To the best of our knowledge, there is little published reports on preparation of low cost indialite glass-

ceramics based on local as silica sand, magnesite and clay raw materials. The main purpose of the present study is to produce Indialite-cristobalite phases which has different characteristics than existed glass-ceramics based on natural raw materials.

RESULTS AND DISCUSSIONS

The DTA traces of the investigated glasses were shown in (Table 1 and Fig. 1) The low intensity exothermic effect in the glass samples were due to slow crystallization. The crystallization peaks were at 1056°C and 1125°C corresponding to samples O and A free nucleating glasses. TiO₂ nucleating agent (samples O-T) reduced the exothermic crystallization peak-temperature by 200°C (1.23%). Addition of LiF decreased the crystallization peaks by 60°C (1.06%). When three nucleating agents such as (TiO₂+LiF+Cr₂O₃) were added to the sample the exothermic value decreased by 314°C (1.42%) as compared to nucleating free glass (sample O). When TiO₂, LiF and TiO₂+ LiF+Cr₂O₃ were added as a nucleating agent in other free glass (sample A) the exothermic crystallization points decreased by 1.48%, 1.05% and 1.46%, corresponding to samples A-T, A-L and A-TLC, respectively.

The XRD patterns of free glass sample O (magnesite + clay + alumina) which was heat-treated at a temperature 900°C/8 hrs through single and double-stage did not show any sign of crystallization of cordierite (Fig. 2 and Table 3). It may be due to their crystal immaturity or insufficiency and were beyond the sensitivity of X-rays. But at higher temperature (1000°C/8 hrs; 1100°C/8 hrs, 850+ 1100°C/8 hrs each and 1100°C/40 hrs) the crystallization of α -cordierite was as principal phase clearly observed.

For other free glass sample A (magnesite + clay+silica sand) and TiO₂ containing samples (O-T) the cordierite phase was also not confirmed at 900° and 1000°C for 8

hrsA, but the crystallization of cristobalite phase was noted. At double stage and single stage treatment with long durations (850+1100°C for 8hrs each and 1100°C for 40hrs) the crystallization of cordierite and indialite was observed clearly. At 900°C to 1000°C/8h the crystallization of anorthite was observed. The presence of more SiO₂ and less Al₂O₃ in A sample as compared to O sample is probably the main reason for forming cristobalite at lower temperature.

Furthermore, crystallization of pseudo-brookite took place at higher temperature (850+1100°C) in TiO₂ containing samples (O-T). When temperature further increased crystallization of cordierite and its meta stable indialite phases was noted at 1100°C/8h & 1100°C/40 hrs. On the otherhand, the XRD peaks intensities of single heat-treated sample were greater than double heat-treatment of the same samples due to fast crystallization. The XRD patterns of A-T samples showed at a higher temperature the crystallization of spinel metastable phase of cordierite was developed. On double stage heat treatment and long durations (850 +1100°C/8 hrs and 1100°C for 40 hrs) the crystallization of α -cordierite was clearly observed which was similar to that of sample O-T. The SiO₂ ratio was probably responsible for the crystallization of spinel at 1100°C/8 hrs. O-L sample showed crystallization of indialite at lower temperature (900°C for 8hrs), at higher temperatures (1000°C, 1100°C/8hrs and 850+1100°C/8hrs each), the domination of cordierite and indialite phases were noticed. But when the duration of heat treatment increased (1100°C for 40 hrs.) the peak intensity of cordierite phase was also increased with the sintering time.

For O-TLC sample the crystallization of α -cordierite was clearly observed at temperatures 1100°/8hrs, 850°+1100°/8hrs and 1100° for 40hrs. A-TLC sample showed crystallization of enstatite at lower

temperature (900°/8hrs) and anorthite at temperature 1000°/8hrs but when temperature increased at 1100°/8 hrs. the crystallization of cristobalite was noticed. At double stage and long duration heat treatment temperature (850+1100°/8hrs and 1100°/40hrs), the crystallization of α -cordierite was observed. The effect of temperature on the crystallization phase is very clear with TLC nucleating agent.

CONCLUSIONS :

- 1 LiF decreases the crystallization temperatures by about 60-350°C as compared to the glass without nucleating agent.
- 2 LiF had little variation in the formation of crystallization and amorphous phases at different heat-treatment stages.
- 3 The optimum Crystallization temperature is 1000°C/6hrs when using local raw materials for glass ceramics production.
- 4 LiTiO₂ affects the crystallization temperature.

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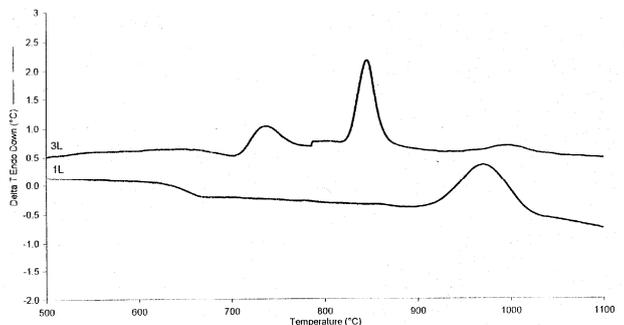
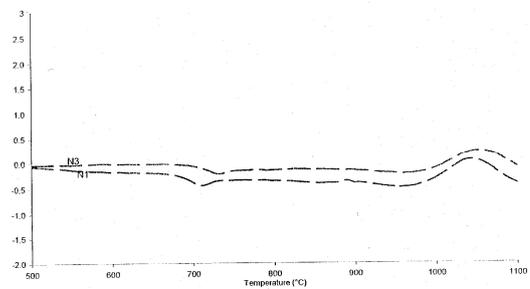


Fig.1 DTA Curves of Base Glass

Table 1: Batch Composition and Nucleating agent

Sample No	Batch compositions	Nucleating (%)
O	M.+C+Al	-----
O-T	M.+C+Al +TiO ₂	TiO ₂ 14.29
O-L	M.+C+Al + LiF	LiF 1.52
O-TLC	M.+C+Al+TiO ₂ +LiF+Cr ₂ O ₃	TiO ₂ +LiF+Cr ₂ O ₃ 14.29+152 +0.59
A	M+C+SS	-----
A-T	M+C+SS+ TiO ₂	TiO ₂
A-L	M+C+SS+ LiF	LiF
A-TLC	M+C+SS+ LiF+Cr ₂ O ₃ +TiO ₂	TiO ₂ +LiF+Cr ₂ O ₃

Table 2: Glass transition and crystallization Temp.

Sample No	Batch Composition	Nucleating agents	GlassTransition tempe(Tg)	Crystallization Peak
O	M.+C+Al	-----	627.161°C	1056.898°C
O-T	M.+C+Al +TiO ₂	TiO ₂	740.968°C	990.714°C
O-L	M.+C+Al + LiF	LiF	586.902°C	1046.722°C
O-TLC	M.+C+Al+TiO ₂ + LiF+Cr ₂ O ₃	TiO ₂ +LiF+ Cr ₂ O ₃	664.130°C	964.410°C
A	M+C+SS	-----	581.412°C	1125.265°C
A-T	M+C+SS+ TiO ₂	TiO ₂	724.693°C	928.716°C
A-L	M+C+SS+ LiF	LiF	361.232°C	1068.964°C
A-TLC	M+C+SS+ LiF+Cr ₂ O ₃ +TiO ₂	TiO ₂ +LiF+ Cr ₂ O ₃	647.909°C	870.809°C