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Physical and chemical characterisation of silica based raw materials from industrial waste

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ABSTRACT Silica sand and Pulverised Fuel Ash (PFA) is considered as silica based waste materials and it have variety of usage depending on its particle size and purity. Value adding of these raw materials will enhance the exploitation of these materials in various industries. The physical and chemical properties of these materials are essential that it will determine the utilization of these materials. The phase analysis, chemical composition, particle size distribution and the morphology of the materials were determined to investigate the appropriate utilization of these raw materials in various applications. Local PFA is considered class F and has various applications as construction materials.

(Silica, Pulverised fuel ash, XRD, XRF, Particle size, Morphology)

INTRODUCTION

The legendary tin mining area such as in Tronoh and Bidor, Perak as well as in Ampang Pecah, Sg. Gumut and Sg. Inki, Selangor is involved extensively on the production of tailing sands, which can be processed, into silica sand. Approximately 65 million tonnes of tailing sand had been identified [1]. Silica sand is mainly used in the glass manufacturing, filter sand in the water treatment, foundry sand and in the chemical and ceramic industries.

Pulverised fuel ash (PFA), also known, as fly ash is the term used to describe the very fine alumino-silicate material (silica based raw material) produced after combustion in coal fired power generation. It is usually captured from the gas flue stream by electrostatic precipitations or wet scrubbing and although some is used in construction, lightweight aggregates and other minor applications, most is disposed of in landfill sites or surface impoundments. Another possible alternative to disposal is the use of PFA for the synthesis of zeolite adsorbents in environmental applications such as the treatment of aqueous effluent and landfill gas. The production of PFA by the local power plant is boosting yearly and in 2005 30% of the power generated in Malaysia will be from coal plant. The world production of PFA from 1987 to 1989 is around 41.5 million tonnes but only 16% of the total production was used in construction sector. Malaysia PFA is utilised as a pozzolanic admixture and stockpiled in embankments around the power stations. According to 8th Malaysia Plan, by the years 2005, Malaysia will consume 11.2 million tonnes of coal per annum and the PFA production will be more than 2 million tonnes [2].

This paper is focusing on the physical and chemical characteristics of the local ex-tin mining silica sand and PFA from the local coal power station waste whether it comply with the industrial needs and certain standards such as ASTM.

Physical And Chemical Characterisation Requirements Of Silica Base Raw Material

Table 1 shows the ASTM Specification for PFA classification according to its chemical composition.

Table 1: ASTM Specification for PFA classification

Chemical composition	ASTM C 618 Specification
Total $SiO_2 + Al_2O_3 + Fe_2O_3$	50.0 % min – Class C 70.0 % min– Class F
CaO	> 10% - Class C < 10% - Class F
SO_3	5.0 % max.
Na_2O	1.5% max.
Loss on ignition LOI	6.0% max.

Table 2 shows the particle size and purity of silica for various application of silica in the industries [3].

Table 2: Silica applications

No.	APPLICATION	Particle Size, μm	PURITY OF SiO_2,%
1	Mechanical Alloying – Powder raw material	>60	99.9
2	High Strength Concrete	Fine powder	none
3	Paint & Coating	5	99.2
4	Thermosets plastics	5	99.2
5	Silicon Rubber	5	99.2
6	Fused Silica		
	- heat resistance	*submicron-1000	99.8
	- epoxy moulding	*submicron-1000	99.8
	- presicion moulding	*submicron-1000	99.8
7	Solar grade silicon	>100	99.999
8	Semiconductor grade silicon	>60	99.999
9	Metallurgical grade silicon	>60	98.0
10	Thin Flim	submicron	99.0
11	Polymer	submicron	99.0

* Depends on application

EXPERIMENTAL

The silica sample was obtained from local ex-tin mining area in Tronoh, Perak where else the PFA sample was obtained from a local coal generated power plant in Kapar, Selangor. These samples undergo the sampling procedure to obtain a representative sample from the bulk. The samples undergo phase identification analysis via X-Ray Diffraction and its chemical composition was obtained via X-Ray Fluorescence method.

Full size analysis of feed samples was conducted following the $\sqrt{2}$ series in the test sieves for the silica sand sample. The particle size distribution of PFA was measured by scattering of laser beam; in this case the Malvern Particle Size Analyser with a size measurement range of 0.1μm to 1000μm as the samples was very fine. The microscopic study was conducted in Scanning Electron Microscope (SEM) to determine the particle morphology.

RESULTS AND DISCUSSION

Figure 1 shows the particle size analysis of the silica sand and PFA sample. The median particle size, d_{50} obtained from the analysis was 1085μm and 6.92μm for silica sand and PFA respectively.

Figure 2 shows the diffraction pattern for silica sample and the standard peak has confirm the sample contents quartz. Figure 3 shows the diffraction pattern for PFA.

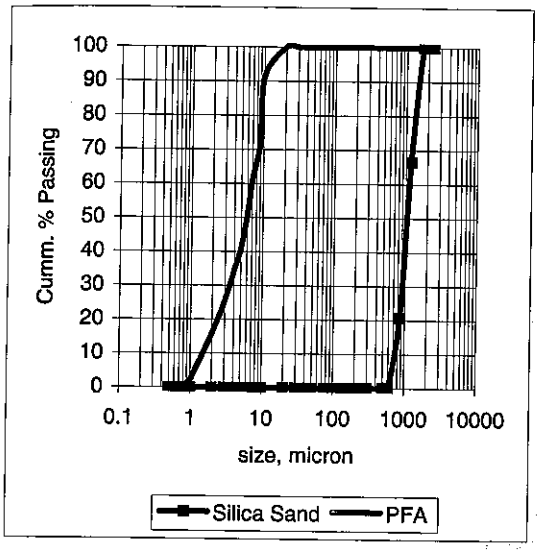

Figure 1. Particle size distribution of silica sand and PFA.

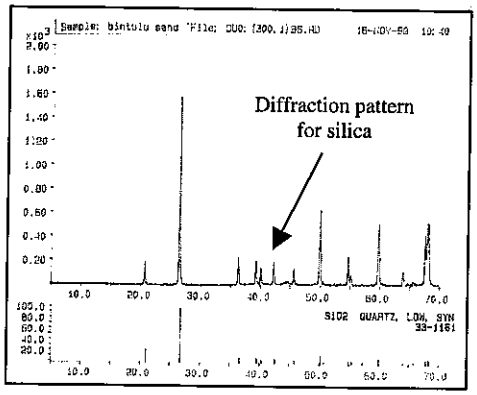

Figure 2. Diffraction pattern of Silica.

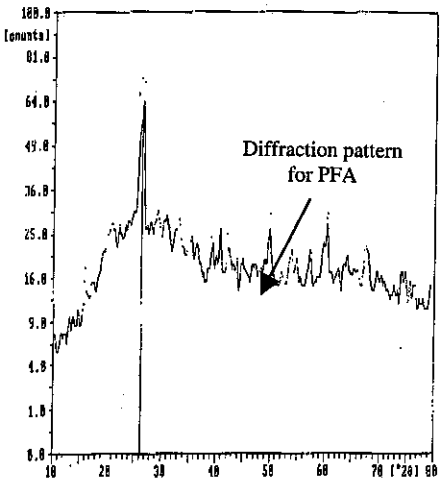

Figure 3. Diffraction pattern of PFA.

Table 3 shows the chemical composition of Silica and PFA. The major constituent in these samples is SiO_2. The SiO_2 content in silica sand and PFA is 99% and 59% respectively. Alumina and calcium oxide content in PFA is 20% and 6.9% respectively but these elements are minor constituents in silica sand sample.

Table 3: Chemical Composition Of Silica and PFA

Elements	SiO_2	Al_2O_3	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	Fe_2O_3	NiO	MgO	LOI
ilica(% wt)	99.00	0.23	0.03	0.01	0.07	0.05	0.03	0.25	0.01	-	-
FA(% wt)	59.0	20.0	1.00	0.90	6.90	-	-	3.70	-	1.40	4.62

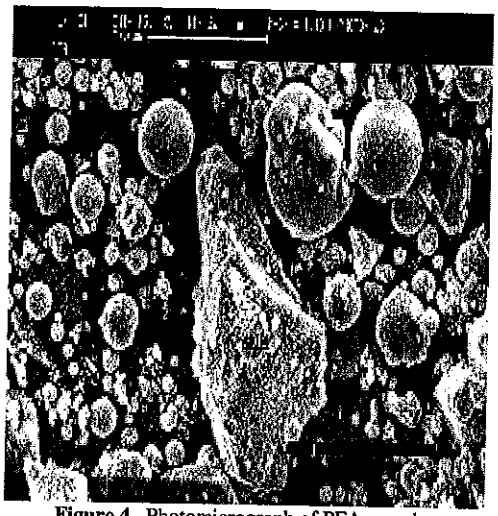

Figure 4. Photomicrograph of PFA sample.

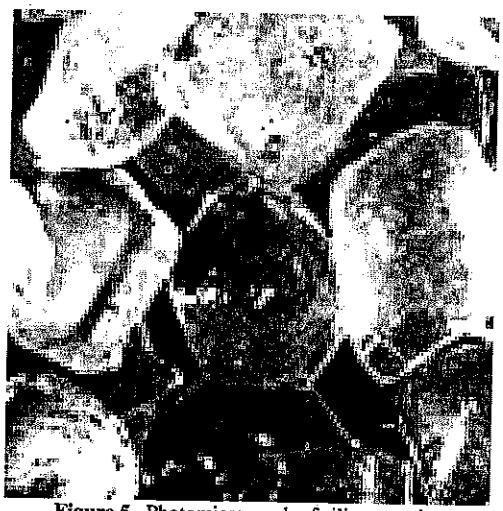

Figure 5. Photomicrograph of silica sample.

Figure 4 shows the photomicrograph of the PFA. It shows that the PFA is a regular spherical (cenosphere) particles and the particle size ranging from 4 μm to 14 μm. Figure 5 shows the photomicrograph of the silica. Silica from the ex-tin mining area is in cubical shape and has a rough surface compare to PFA, which has a smooth surface.

CONCLUSION

The silica based waste materials such as the silica sand from ex-tin mining area and PFA from the local has a versatile usage in various industries such as the used in the glass manufacturing, filter sand in the water treatment, foundry sand and in the chemical, ceramic industries, construction, lightweight aggregates and other minor applications, most is disposed of in landfill sites or surface impoundments. Recycling of these waste materials will help to solve the environmental problem as well as enhance the growth of the recycling and mineral industries. The silica sand sample from ex-tin mining area can be use for glass manufacturing, filter sand in the water treatment, foundry sand and in the chemical, ceramic industries and constructions. Value adding of the silica in terms of particle size and purity will enhance the properties of these materials and it can be used as a feedstock for advance materials applications. Where else the PFA comply the standard ASTM Class F. It can be used as a raw material for lightweight aggregate production, as additional composition in cement., as a replacement for the fine aggregates in concretes and mortar and as constituent of lightweight aerated concrete for the construction of insulating building block.

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Synthesis of strontium-doped barium titanate

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ABSTRACT Strontium (Sr)-doped Barium Titanate ($Ba_{1-x}Sr_xTiO_3$) is a versatile electroceramic that has widespread applications. The doping of Sr has enable high permittivity to occur at room temperature by lowering the curie temperature (T_c) in the system. In this paper, single phase $Ba_{0.85}Sr_{0.15}TiO_3$, $Ba_{0.70}Sr_{0.30}TiO_3$ and $Ba_{0.55}Sr_{0.45}TiO_3$ were successfully synthesized using conventional mix-oxide method. The X-Ray Diffraction (XRD) analysis indicates that the interplanar spacing value (d-value) decreased as the Sr content increased in the sample.

Strontium, Barium Titanate, XRD)

INTRODUCTION

Electroceramics with high permittivity have been in great demand for insulators, capacitors and other applications. Barium Titanate ($BaTiO_3$) is one of the most commonly used electroceramics in the industry because of its high permittivity property. At room temperature, $BaTiO_3$ is a ferroelectric material with tetragonal perovskite structure (Figure 1); it has the maximum permittivity at temperature close to T_c (about 395K). Above the T_c, $BaTiO_3$ is in paraelectric state with cubic structure (Figure 1) [1]. However, in order to meet certain applications, $BaTiO_3$ is rarely used without any chemical modification. Chemical modifications such as isovalent substitutions, acceptor dopants and donor dopants are possible to modify the original properties of $BaTiO_3$. The incorporation of Sr, one of the isovalent ions for Barium (Ba), reduces the T_c of the original $BaTiO_3$ system [2]; therefore making it possible to produce $Ba_{1-x}Sr_xTiO_3$ with high permittivity with the T_c close to room temperature by controlling the Sr concentration and meets the appropriate application [3]. Hilton and Ricketts [4] had reported that the T_c shifted to 310K as $BaTiO_3$ was doped with 0.3mol% of Sr to form $Ba_{0.70}Sr_{0.30}TiO_3$. This paper reports the synthesis of single phase $Ba_{1-x}Sr_xTiO_3$ at the x value of 0.15, 0.30 and 0.45 mol%.

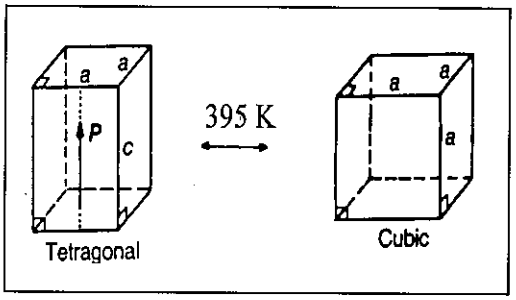

Figure 1. Unit Cell of $BaTiO_3$

MATERIALS & METHOD

$Ba_{1-x}Sr_xTiO_3$ with compositions of x = 0.15, 0.30 and 0.45 were prepared by conventional solid state, mix-oxide route. Barium Carbonate ($BaCO_3$, Merck, purities >99%), Strontium Carbonate ($SrCO_3$, Merck, purities >99%) and Titanium(IV) Dioxide (TiO_2, Merck, purities >99%) were weighted out in stoichiometric proportion. The chemicals were mixed by dry ball milling for 16 hours using zirconia balls in respective polyethylene bottles. The mixtures were calcined at 1300°C for 3 hours. All the samples were ground to fine powder using agate mortar and pestle and analyzed by XRD (Philips, PW1710 copper anode) to determine the phases.

RESULTS AND DISCUSSION

The samples ($Ba_{0.85}Sr_{0.15}TiO_3$, $Ba_{0.70}Sr_{0.30}TiO_3$ and $Ba_{0.55}Sr_{0.45}TiO_3$), after calcined at 1300°C for 3 hours, were off-white. Both $BaCO_3$ and $SrCO_3$ were decarbonated at > 900°C to form Barium Oxide (BaO) and Strontium Oxide (SrO) [5]:

$$BaCO_3\ (s) \rightarrow BaO\ (s) + CO_2\ (g) \quad (1)$$

$$SrCO_3\ (s) \rightarrow SrO\ (s) + CO_2\ (g) \quad (2)$$

Both BaO and SrO were reacted with TiO_2 to produce a single phase $Ba_{1-x}Sr_xTiO_3$ at high temperatures (approximate 1150°C) [6]. Figure 2 shows the diffractograms of the samples synthesized. The solid state reaction proceeded entirely to form the single phase $Ba_{0.85}Sr_{0.15}TiO_3$, $Ba_{0.70}Sr_{0.30}TiO_3$ and $Ba_{0.55}Sr_{0.45}TiO_3$.

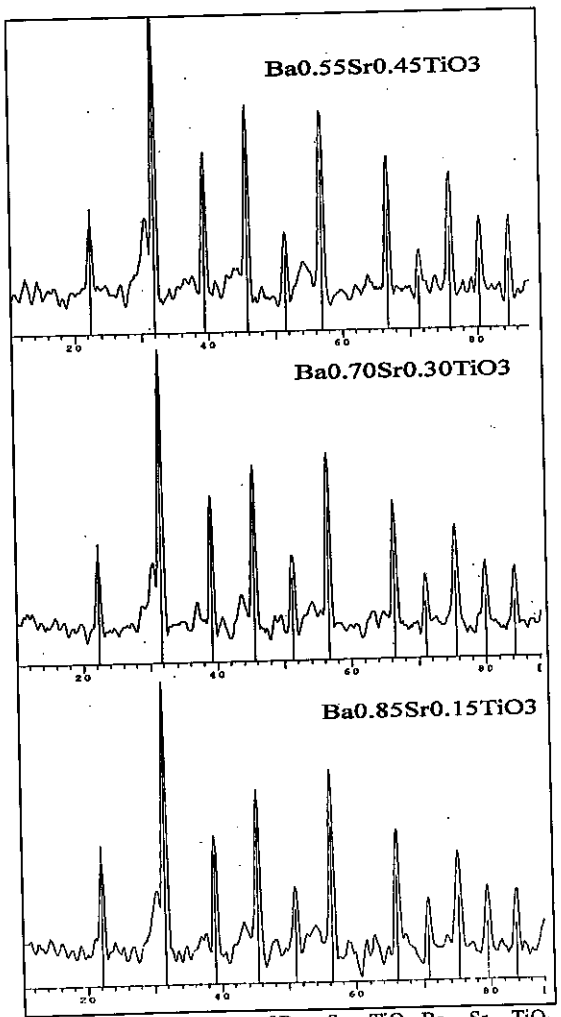

Figure 2. Diffractograms of $Ba_{0.85}Sr_{0.15}TiO_3$, $Ba_{0.70}Sr_{0.30}TiO_3$ and $Ba_{0.55}Sr_{0.45}TiO_3$

Table 1 shows the interplanar spacing value (d-value) of each sample. The d-value of each sample decreased with the increased of Sr content in the samples. Strontium ions (Sr^{2+}), which has similar charge to Barium ions (Ba^{2+}), can dope into $BaTiO_3$ perovskite crystal structure lattice quite readily. The d-value changes may be correlated with the ionic radii of both Sr^{2+} and Ba^{2+}. It appears that the smaller Sr^{2+} (ionic radii of 1.13Å) causes a contraction of the unit cell relative to Ba^{2+} (ionic radii 1.35Å) when it is doped. The higher concentration of Sr^{2+} (higher x value) in the sample will cause more severe distortion in the unit cell itself, this resulted a larger shift in d-value.

Table 1: d-value for $Ba_{0.85}Sr_{0.15}TiO_3$, $Ba_{0.70}Sr_{0.30}TiO_3$ and $Ba_{0.55}Sr_{0.45}TiO_3$.

d-value (Angstrom)		
$Ba_{1-x}Sr_xTiO_3$		
x = 0.15	x = 0.30	x = 0.45
3.9992	3.9754	3.9701
2.8233	2.8125	2.8009
2.3050	2.2960	2.2876
1.9948	1.9886	1.9810
1.7864	1.7790	1.7733
1.6298	1.6237	1.6166
1.4118	1.4056	1.4004
1.3306	1.3254	1.3210
1.2614	1.2574	1.2518
1.2034	1.1985	1.1935
1.1527	1.1476	1.1430

CONCLUSION

Single phase $Ba_{0.85}Sr_{0.15}TiO_3$, $Ba_{0.70}Sr_{0.30}TiO_3$ and $Ba_{0.55}Sr_{0.45}TiO_3$ were successfully synthesized by solid state reaction. The XRD analysis shows the d-value of the samples decrease with the increase of Sr content (x value) in the system.

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