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Preparation of Alexandrite by the Sol–Gel Process and Its Characterisation

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Abstract: Alexandrite is an important material which finds applications in many spheres of science and engineering. It is present in nature as a mineral called "chrysoberyl". But as its occurrence is limited and impure, this mineral has been produced synthetically to meet various requirements.This paper describes a sol–gel method of preparation of this mineral based on citrate gel processing and identifies the advantage of this method over the conventional macroscopic method. The gel formed by this process is pyrolysed at various temperatures and the powders obtained are characterised by XRD, SEM and particle size analysis. The diffraction characteristics of the samples sintered at different temperatures up to the melting point of the mineral so formed are examined and discussed with respect to the phase diagram of BeO–Al_2O_3 system. It is found that at 1000°C alexandrite phase is obtained and it changes only after further heating up to the melting point, 1800°C.

1 INTRODUCTION

Alexandrite is a double oxide of beryllium and aluminium. The chemical formula is $Be(AlO_2)_2$ or BeO,Al_2O_3. It occurs in nature as a mineral called chrysoberyl. In monocrystal form, doped with chromium oxide, this binary oxide is known to be used as a laser active medium to generate tunable lasers. One of the earliest applications[1] of the alexandrite laser was in atmospheric sensing, for detection of water vapour and oxygen concentrations at wavelengths of 724 and 760 nm, respectively.

Subsequently, alexandrite lasers have been applied on laser isotope separation. The wavelength response of silicon cameras peaks near the central operating wavelength (700–800 nm) of the alexandrite laser. Thus, the laser can be used as an efficient illumination source for silicon cameras. It is also used in spectroscopy, medicine, materials treatment, semiconductors annealing, etc. Further, synthetic crystals of alexandrite, grown by pulling from solution-melt, are used to manufacture jewellery insets because of their fascinating colours.

Alexandrite is reported[2] to be prepared by heating beryllium oxide and aluminium oxide at 1300°C and reheating it again, after grinding, to 1400°C. In an earlier paper,[3] a description is given of how alexandrite was synthesised macroscopically starting from beryllium oxide and aluminium oxide powders with chromium oxide doping. It is called macroscopic here because the sources of beryllium and aluminium oxides were from precipitation, which gives rise to large particles. Besides, the mixing mechanism of oxides followed there was totally mechanical and not on a molecular level.

The citrate gel process has been used to prepare ceramics of high purity, high chemical homogeneity and small particle size.[4–8] Adopting this process, as described in this paper, we have tried to find out how suitable the sol–gel method is to produce alexandrite and whether there is any benefit to use this process over the above mentioned conventional macroscopic method. Characterisation of this product has been carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) and particle size analysis. The XRD patterns of the product are examined after pyrolysing it at various temperatures up to its melting point. The diffraction characteristics and melting temperature are discussed in the light of the phase diagram of the BeO–Al_2O_3 system.

2 EXPERIMENTAL PROCEDURE

2.1 *Preparation of the citrate gel precursors*

In this scheme, precursors corresponding to approximately 10 g of alexandrite were prepared. Analar grade citric acid (99.5%) and aluminium nitrate (98.5%) were dissolved separately in 100 ml of distilled water, taking 44.29 g and 59.87 g, respectively. Beryllium nitrate was prepared from BeO (99.9%). For this, 5 g of beryllium oxide was converted to sulphate by fuming with electronic grade sulphuric acid. The beryllium sulphate was dissolved in distilled water and beryllium hydroxide was precipitated out of it with the help of ammonia solution. The hydroxide was converted to nitrate by treating it with 14 ml of nitric acid (69.5%) and making up the volume to 100 ml by adding distilled water. From the above beryllium nitrate solution, only 39 ml was taken. This was put in a beaker and 100 ml each of aluminium nitrate and citric acid solutions were added to it separately with continuous stirring. After stirring for 15 min the mixture was heated at 75–80°C till a thick paste was formed. This thick paste was found to become thin on cooling.

2.2 *Thermal decomposition of the precursors and sintering*

The precursors in the paste form obtained above were dried in a muffle furnace at 150°C. Decomposition of this product and colour changes thereby were studied by heating it both rapidly (10°C min^{-1}) to 1000°C and slowly (2°C min^{-1}) in stages to 200, 350, 550 and 650°C. Finally, the decomposition products were heated or sintered at 400, 650, 850, 1000, 1500 and 1800°C for 4 h, 4 h, 2 h, 1 h, 20 min and 30 min in a muffle furnace and induction furnace, respectively. The temperatures in the muffle furnace were measured by a thermocouple, whereas those in the induction furnace were measured by a two colour optical pyrometer.

2.3 *Characterisation of precursors and oxide products*

X-ray diffraction analysis was carried out using a diffractometer, Diano Series 2000, USA, to characterise the precursors after heating at 400°C and its products of decomposition after sintering at 650, 850, 1000, 1500 and 1800°C. Particle size and distribution pattern of the powders were found out by a Horiba LA-500 model, Japanese particle size analyser and the morphology of the particles obtained after heating the powder to 1800°C was determined by SEM (Cambridge Instruments, Sterioscan S-240, UK).

A platinum crucible (for sintering) and agate mortar and pestle (for grinding of sintered samples) were used to avoid any cross-contamination which could affect the XRD and SEM analysis. For heating at 1500 and 1800°C, beryllia crucibles were used. For particle size analysis, the powders were ultrasonically treated, for half an hour each, in a 0.1% aqueous solution of calgon to disperse the particles.

3 RESULTS AND DISCUSSION

3.1 *Precursor characterisation and decomposition temperature schedule*

The precursors were found to form a thick paste while hot, after evaporating the mixed solution at 75–80°C. But on cooling, its viscosity appeared to be reduced, making it relatively thin. After drying this gel at 150°C, the powder obtained was spongy, hygroscopic and pale yellowish-white in colour. This powder turned to black when heated rapidly to 1000°C at a rate of 10°C min^{-1}. This black colour did not change, even after heating at a higher temperature. This is due to charring of citrates to carbon. To avoid this, decomposition was carried out slowly by heating the gel at a rate of 2°C min^{-1} when the colour of the powder changed, as shown in Table 1. From this table it is seen that colour change started at 200°C and completed at 650°C. The slow heating ensured complete conversion of citrate into carbon dioxide, which was a basic need to avoid carbon contamination in the oxide product later.

The precursor, even after heating at 400°C for 4 h, remained dark brown or black. The *d*-values of

Table 1. Change of colour of precursor by thermal decomposition

Sr. no.	Temperature (°C)	Colour
1	Below 200	Pale yellowish-white
2	200	Light brown
3	350	Dark brown
4	550	Starts to change to white
5	600	Mostly white with brown tinge
6	650	Completely white

X-ray diffraction of this sample are shown in Table 2. It has only two *d*-values, which indicates that the sample is amorphous and does not have distinct peaks characteristic to the material.

3.2 Characterisation of oxide products

3.2.1 X-ray diffraction studies

The XRD data of the samples sintered at 650, 850 and 1000°C are shown in the Tables 3, 4 and 5, respectively. Table 3 indicates only 5 *d*-values for the sample heated at 650°C. In this case also, it was not possible to identify the peaks in the XRD pattern. This means that at 650°C, the sample is still amorphous. Table 4 corresponds to the sample sintered at 850°C. The XRD pattern of this sample indicated that the crystallinity of the sample did appear with definite peaks at 850°C, but the *d*-values did not match those of alexandrite. The *d*-values in Table 5, where the XRD data of the sample sintered at 1000°C have been indicated, match well to the *d*-values of the powder diffraction file data of alexandrite. The diffraction patterns of the samples sintered at 1500 and 1800°C were also taken. It was seen that the pattern and the *d*-values of the sample at 1500°C remained the same as those of the sample sintered at 1000°C. This indicates that although alexandrite has formed at 1000°C, it remained unchanged up

Table 2. XRD data of precursor heated at 400°C

Peak no.	*d*-value(A°)	I/I_{max}(%)
1	4.4098	100.00
2	4.3562	79.72

Table 3. XRD data of the sample heated at 650°C

Peak no.	*d*-value(A°)	I/I_{max}(%)
1	4.4055	100.00
2	4.2651	96.33
3	2.2829	46.95
4	2.1757	44.44
5	1.8040	35.12

Table 4. XRD data of the sample sintered at 850°C

Peak no.	*d*-value(A°)	I/I_{max}(%)
1	3.7676	43.28
2	3.2530	100.00
3	2.6471	54.29
4	2.4695	64.42
5	2.2949	39.89
6	2.1777	39.89
7	2.1313	25.00
8	2.0011	29.10
9	1.9160	30.54
10	1.7358	21.21
11	1.5818	25.00
12	1.5277	22.44
13	1.5013	17.73
14	1.4476	17.73
15	1.3822	17.73
16	1.3331	23.70
17	1.2802	21.21

Table 5. XRD data of the sample sintered at 1000°C

Peak no.	*d*-value(A°)	I/I_{max}(%)
1	4.0002	45.56
2	3.5360	12.84
3	3.2196	68.06
4	2.5560	49.00
5	2.3591	12.84
6	2.3145	29.34
7	2.2565	50.17
8	2.2343	9.51
9	2.0858	100.00
10	2.0720	49.00
11	1.8683	9.51
12	1.7808	7.11
13	1.6607	10.56
14	1.6480	12.25
15	1.6155	79.51
16	1.5438	10.56
17	1.5061	7.11
18	1.4597	12.84
19	1.3686	19.51
20	1.3597	25.84
21	1.3124	7.11
22	1.2955	9.51
23	1.2846	11.11
24	1.2514	10.56
25	1.2071	7.11

Table 6. XRD data of the sample heated up to 1800°C

Peak no.	*d*-value(A°)	I/I_{max}(%)
1	6.5320	20.25
2	6.4561	16.58
3	4.3700	17.16
4	4.3331	24.29
5	3.9825	36.00
6	3.7938	10.33
7	3.3404	18.98
8	3.2565	14.33
9	3.2202	48.01
10	2.6212	41.33
11	2.6064	78.45
12	2.5514	47.02
13	2.5395	40.41
14	2.3116	22.90
15	2.2533	25.72
16	2.1752	100.00
17	2.0842	41.33
18	2.0711	43.18
19	1.8961	14.88
20	1.6141	45.08
21	1.6092	28.70
22	1.4608	11.76
23	1.3593	23.59

to a temperature of 1500°C. It may be pointed out here that in the literature,[1] and also in a previous investigation,[3] the minimum temperature at which alexandrite phase was obtained in macroscopic synthesis was 1300–1500°C. This means that in the present sol–gel synthesis the alexandrite phase has been obtained at a much lower temperature (1000°C only). So, the sol–gel method or citrate gel route has a definite advantage of lower temperature of synthesis of alexandrite over the earlier macroscopic approach.

The XRD *d*-values, corresponding to intensities higher than 10%, of the sample heated up to 1800°C, are shown in Table 6. From this table it is seen that although most of the peaks that appeared here are common to those of alexandrite, a number of new peaks are also obtained in this case. Further, the intensities of the peaks have also changed to a great extent. This shows that the alexandrite phase, which formed at 1000°C and remained unchanged up to 1500°C, showed a definite change at 1800°C, giving rise to additional peaks. It was also observed during the experiment that the alexandrite pellet, which was heated and found intact even up to 1500°C, no longer remained in the pellet form after heating at 1800°C. On the contrary, it spread into a fused mass at the bottom of the beryllia crucible in which it was heated. This mass was extremely hard and couldn't be removed from the beryllia crucible, either by digging or by heating up to 850°C. It was ultimately transferred to another beryllia crucible by keeping the first crucible inverted on the second crucible and heating both together inside an induction furnace up to 1800°C. In this case, the product after cooling to room temperature was obtained as a powder inside the second crucible. It clearly indicated that at 1800°C the mass in the first crucible melted and got transferred to the second crucible by gravitational force. From the phase diagram of the BeO–Al_2O_3 system (Fig. 1)[9] it is seen that when BeO and Al_2O_3 are present in the molar ratio of 1:1, which is the alexandrite composition, complete liquid phase occurs at 1870°C. This temperature appears to be slightly higher than the experimental temperature of 1800°C at which alexandrite was found to melt. Thus, XRD data shown in Table 6 corresponds to a phase obtained from alexandrite by melting it at 1800°C and resolidified on cooling. Comparing Table 5 and Table 6 it is seen that the *d*-values corresponding to 100% intensity are 2.0858Å and 2.1752Å for the oxide products heated up to 1000 and 1800°C, respectively. All these indicate a possible phase transformation of alexandrite at 1800°C.

3.2.2 Particle size and morphology studies

Figures 2 and 3 indicate the particle size distribution graphs of the products heated at 400 and

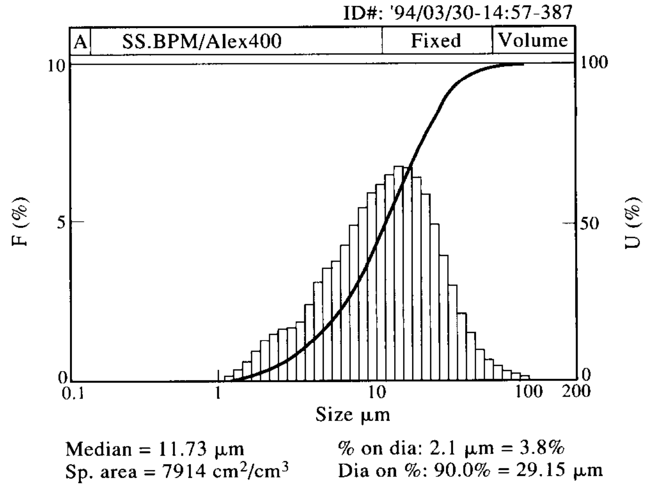

Fig. 2. Distribution graph at 400°C.

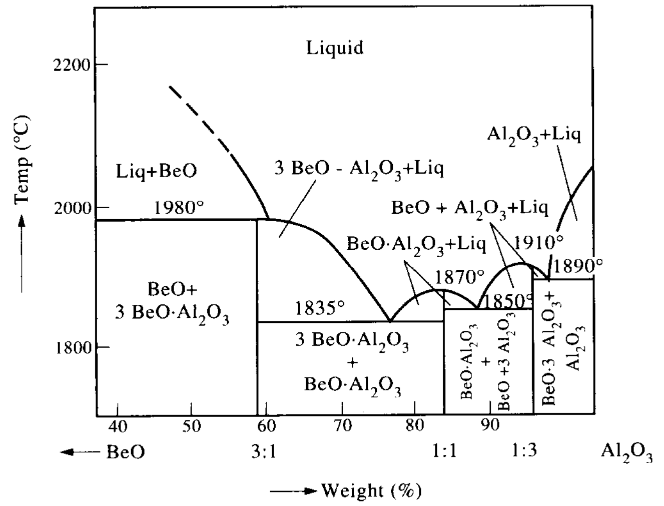

Fig. 1. BeO–Al_2O_3 system.

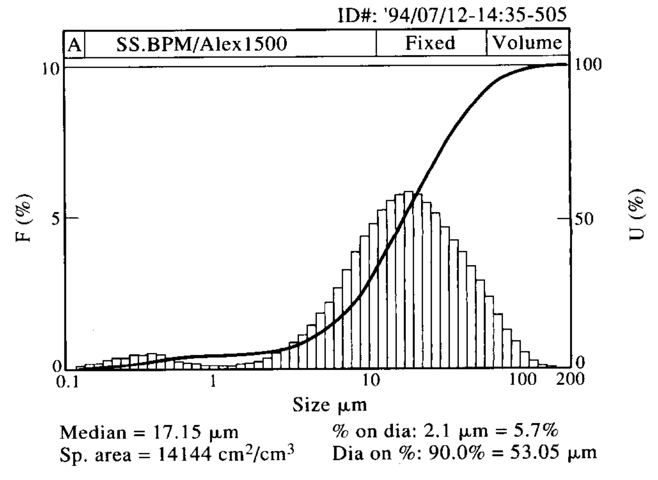

Fig. 3. Distribution graph at 1500°C.

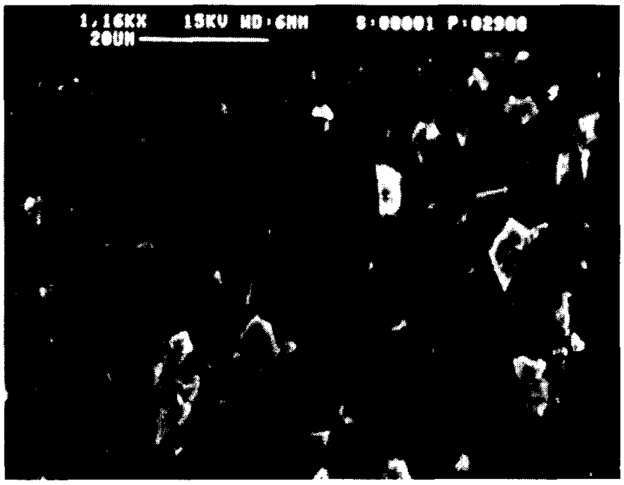

Fig. 4. SEM image showing flake and pellet morphology.

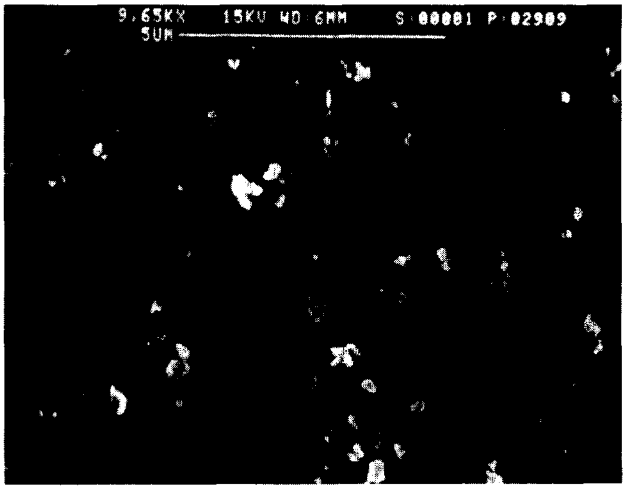

Fig. 5. SEM image showing submicron sized particles with agglomerates.

1500°C. These two temperatures have been chosen in order to compare the characteristics of the particles of the products in the amorphous and crystalline forms, before and after forming alexandrite, respectively. These figures indicate the particle size distributions measured at a particular instant from the suspension. The distribution of the same sample sometimes varies a little if different readings are taken. The median value of particle size, specific surface area of the sample, weight percent of particles of diameter 2.1 μm present in the sample and maximum diameter of 90% particles are shown in these figures. The specific surface area of the powders has also increased from 2133 cm^2/g to 3812 cm^2/g for the alexandrite formed later at the higher temperature. The weight percent of the particles of alexandrite having diameter 2.1 μm is also higher. From this discussion, it can be inferred that after sintering at a temperature of 1500°C, not only was the alexandrite phase formed at 1000°C sustained, the size of the particles also reduced significantly. The grinding process also became easier by sintering at higher temperature.

The SEM images in Figs 4 and 5 indicate the morphology of the product at 1800°C, taken with different magnifications of the same sampling spot. From these figures it is clear that the product is flake type and the minimum size of the particles is on a submicron level, whereas others are agglomerates.

4 CONCLUSIONS

The following conclusions can be drawn from the work reported in this paper.

1. The citrate gel route has been proved to be better at producing alexandrite due to lowering of the sintering temperature from 1300–1500°C to 1000°C.
2. Alexandrite formed at 1000°C was found to sustain its phase up to 1500°C. A phase change was observed in the resolidified oxide after heating alexandrite up to 1800°C.
3. Alexandrite was found to melt at 1800°C, which is slightly lower than the corresponding temperature of 1870°C indicated in the phase diagram of BeO–Al_2O_3.
4. The particle size and sinterability of the oxide powders depend upon the temperature of pyrolysis used.

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