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Soft chemistry synthesis, crystal structure and micro-structural properties of calcium-barium selenate with -AB_2X_5 structure

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ABSRACT

Acetate - citrate precursors were applied to synthesize amorphous gelatinous calcium barium selenate with molecular formula ($Ca_{0.5}Ba_{0.5}Se_2O_5$).The gel-product was sintering at 800°C for two hrs then well characterized by X-ray diffraction , SEM and EDX elemental analyses and proved that the product $Ca_{0.5}Ba_{0.5}Se_2O_5$ is mainly belong to AB_2X_5-type structure with average grain size ranged in between 1.2 -3.8 µm .A visualized study was constructed to confirm the molecular structure of calcium-barium selenate .

Keywords : Sol-Gel Synthesis, Selenates, X-ray diffraction, SEM, Crystal Structure.

INTRODUCTION

Many researchers investigated synthesis of elemental selenium, metal selenate or selenite due to their unique structural, biological features and medicinal applications of these selenium containing compounds [1-11].

Nishimura et al.[12] investigated the equilibrium between phases of Fe_2O_3–SeO_2–H_2O system by allowing amorphous ferric selenite ($Fe_2(SeO_3)_3 \cdot 4H_2O$) precipitate to react with a solution of selenious acid (H_2SeO_3) at 25 °C. Giester et al.[13] estimated the crystal structure of iron(III) selenate(IV) trihydrate, $Fe_2(SeO_3)_3$. $3H_2O$ by means of single-crystal X-ray diffraction methods and found that ferric selenate is mainly belongs to R3c space group, with lattice constant a =9.3601 A° ,c = 20.2972 A° .Also they found that $Fe_2(SeO_3)_3$. $3H_2O$ is isotypic with the analogues Al, Ga and Cr compounds. Ktari et al. [14] have studied crystal structure of the thallium selenate tellurate $Tl_2SeO_4 \cdot Te(OH)_6$ (TlSeTe) by X-ray diffraction method .They reported that thallium selenate crystallizes in the monoclinic system with $P2_1/c$ space group and the lattice parameters were: a = 12.358(3) Å; b = 7.231(1) Å; c = 11.986(2) Å .

Baur et al.[15] synthesized ($3CaO \cdot Al_2O_3 \cdot CaSeO_4 \cdot xH_2O$) and characterised it by bulk chemical analysis and X-ray diffraction.

The essential goal of the present study is to investigate capability of synthesizing ca-barium selenate with AB_2O_5 structure type via application acetate-citrate sol-gel route where barium and calcium on the same site $Ca_{0.5}Ba_{0.5}Se_2O_5$ and visualization of molecular structure to confirm structure type which is AB_2X_5.

MATERIALS AND METHODS

2.1. Materials and reagents:

The following materials and reagents were used: citric acid (Aldrich, 99%, $C(OH)(COOH)(CH_2COOH)_2$), ammonia (UCB, p.a. NH_3 ca. 25% in H_2O), Selenium(IV)nitrate , ammonium oxalate), hydrogen peroxide (Acros Organics, 35 wt.% solution in water, stabilized, H_2O_2), barium acetate (Aldrich, 99.995%, $Ba(CH_3COO)_2$), calcium acetate (Aldrich, 99.99+ %) and acetic acid (UCB, 99–100%, p.a., 1.049 kg/L, CH_3COOH).

2.2. Aqueous solution–gel synthesis of the CBS- acetate–citrate gel:

To start with, the aqueous solution–gel synthesis of multi-metal oxides requires the preparation of a stable, clear and homogeneous precursor solution containing the different metal ions. Moreover, upon solvent evaporation this solution must be converted into an amorphous gel maintaining the homogeneity on atomic scale. . A 0.3 mol/L Se-precursor was synthesized by dissolution of Se (IV) ammonium oxalate in an aqueous solution of citric acid and hydrogen peroxide (the oxalate is decomposed by reaction with H_2O_2).

A 0.1 mol/L aqueous calcium precursor solution was prepared by dissolving of calcium acetate in glacial acetic acid, followed by dilution with water. In order to obtain a stable solution, an amount of 10 mL CH_3COOH was necessary to dissolve 1.2 g Ca -acetate. A barium acetate solution (0.3 mol/L) was synthesized by dissolving barium acetate in water. The exact precursor metal concentrations were measured by means of ICP-AES, using a Perkin-Elmer Optima 3000 DV.

The tri-metallic CBS precursor solution was obtained by mixing the monometallic solutions in stoichiometric amounts. In order to prevent precipitation (of Ba and Ca), an excess of citric acid had to be added until the citric acid: metal ion molar ratio was equal to 3:1 and the pH had to be increased by the addition of ammonia until 4.8.

The synthesized precursor solution was poured out in a vessel and the solvent was evaporated in a furnace at 110 °C under flowing air. The resulting gel was shiny colorless to white and amorphous. The gel was however rather hygroscopic and hence sticky. In order to allow the gel to be removed from the vessel, it needed a further heating step at 160 °C and finally sintering step at 800 ^{o}C for two hrs.

RESULTS AND DISCUSSION

3.1.X-ray Diffraction and Phase Identification:

The XRD patterns of $Ca_{0.5}Ba_{0.5}Se_2O_5$ are shown in Fig.1. All detectable peaks $Ca_{0.5}Ba_{0.5}Se_2O_5$ phase are indexed by red circles, which are matched and compared with the ASTM standard cards and ICSD-data bank (Karlesruhe-Germany).

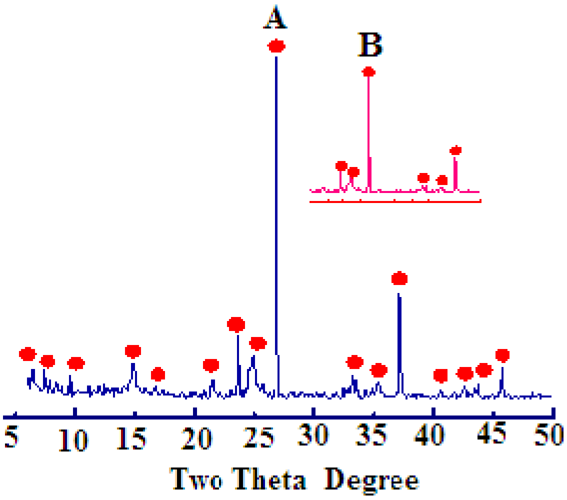

Fig.1. X-ray diffraction pattern recorded for $Ca_{0.5}Ba_{0.5}Se_2O_5$
A. Sol-Gel route synthesis B. Solid State Route ref.[16]

Analysis of the corresponding 2θ values and the interplanar spacings d (A^o) by using computerized program proved that the compound $Ca_{0.5}Ba_{0.5}Se_2O_5$ is mainly belongs to orthorhombic structure type with rhombohedra crystal form and Pbca space group , that expressed by assigned red circles peaks. The unite cell dimensions were calculated using parameter of the most intense X-ray reflection peaks and found to be a = 6.4711 , b= 14.5612 A^o and c = 10.1914 A^o for the pure $Ca_{0.5}Ba_{0.5}Se_2O_5$.

XRD-profile symbolized by A in fig .1 is for $Ca_{0.5}Ba_{0.5}Se_2O_5$ synthesized by means of acetate-citrate sol-gel route and B is for those reported by [16] for $CaSe_2O_5$ compound that prepared via solid state reaction route . The analysis of peak positions between both profiles are nearly identical which means barium replaced calcium sites successfully.

It is well known that minimal criteria of successful substitutions were reported by [17-18] which are ;1st the secondary phases should not grow systematically with propagation of dopant ratio concentration in the solid state solution and special care must be apply to peak indexing of impurity phases, 2nd the shift of lattice parameter of by more than three standard deviations in least squares lattice parameter refinements in the series of doped samples should be seen.,3rd the physical properties of should change on doping or substitutions process and 4th feature must be present in the dopant atom as precondition factor to substitute successfullly ,which is atomic size of the dopant element must be harmonize and thermodynamically compitable with the solid solution of system on doping whatever this system.

Accordingly as clear in Fig.1 barium as doping element substitute successfully on the calcium sites reflecting that all criteria of successful substitution[17-18] are achieved together on barium .

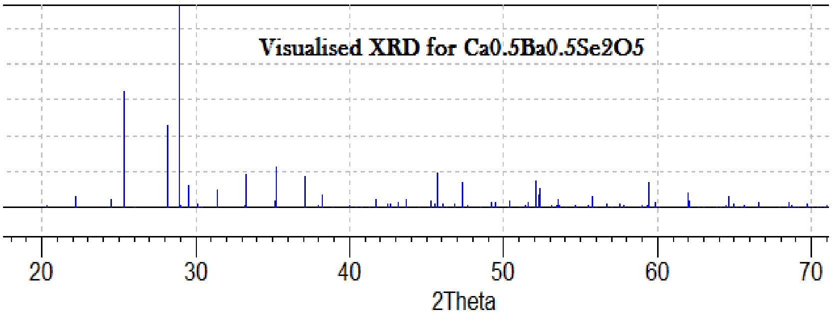

Fig.2. Visualized XRD-profile for $Ca_{0.5}Ba_{0.5}Se_2O_5$ compound

Confirmation of synthesized $Ca_{0.5}Ba_{0.5}Se_2O_5$ compound structure was performed through theoretical treatment by visualizing of structures of both experimental and theoretical lattice coordinates via Diamond Impact Crystal Molecular Structure Version 3.2-visulizer.

A visualization study made is concerned by matching and comparison of calculated theoretical data as bond distances , oxidation states and bond torsion on the crystal structure formed .The study and comparison between XRD-profile Fig.1 and Fig.2 exhibited good fitting of peak positions between experimental and theoretical data confirming that barium substitutes successfully on crystal structure on calcium sites.

The analysis of calculated bond distances shows that there are two types of selenium atoms symbolized by Se-1,Se-2 and one type of calcium - barium atoms (Ca1/Ba1) and finally five types of oxygen atoms symbolized O1,O2,O3,O4and O5.

These types of atoms are classified according to surrounding environment and the calculations were made on the visualized crystal form as shown in Fig.3 with input data file for $Ca_{0.5}Ba_{0.5}Se_2O_5$ compound, orthorhombic structure type with rhombohedra crystal form and Pbca space group and The unite cell dimensions are a = 6.4711, b = 14.5612 A^o and c = 10.1914 A^o for the pure $Ca_{0.5}Ba_{0.5}Se_2O_5$.

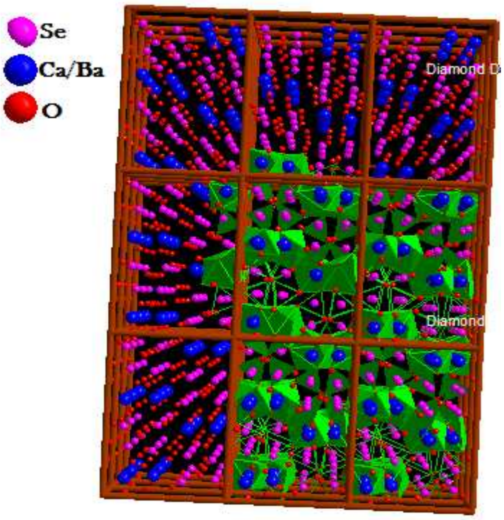

**Fig.3 3x3 super-lattice cell for $Ca_{0.5}Ba_{0.5}Se_2O_5$ compound
2x2 super-lattice shows polyhedral connectivity**

Table.1

Type of Atom Connected	Average of Bond Distance A°
Se1-O1	1.6638
Se1- O3	1.8013
Se1- O2	1.6649
Se2-O3	1.8563
Se2-O4	1.6421
Se2- O5	1.6853
Ca1|Ba1-O	$^{min.}$2.3434 - 2.4833$^{max.}$

The calculated bond distances were listed as shown in Table .1 and compared with data reported in literature [19-22]. It was observed that the present data are compatible with these data with respect to the average recorded for bond distances but contradict in the final crystal form formed.

Lui et al.[19] studied synthesis of rare-earth selenate and selenite materials under "sol–gel" hydrothermal conditions of $La(HSeO_3)(SeO_4)$ and $KNd(SeO_4)_2$ and deduced that $La(HSeO_3)(SeO_4)$ and $KNd(SeO_4)_2$ crystallize in the monoclinic system that contains puckered polyhedral layers made of LaO_x (x = 9,10) and SeO_4 groups, which are connected via SeO_3-uints to the 3D structure like those polyhedral with green color in Fig.3 but the presented selenate is in orthorhombic crystal form.

The simplest crystal structure of selenate is $BeSeO_4·4H_2O$ [20] which crystallizes in the orthorhombic space group *Cmca* and is composed of isolated $Be(H_2O)_4$ and SeO_4 tetrahedral which are interconnected by strong hydrogen bonds with O_w...O lengths between 2.619 and 2.661 Å.

3.2. Scaning Electron Microscopy :

The SEM micrograph of the prepared sol-gel $Ca_{0.5}Ba_{0.5}Se_2O_5$ compound is shown in Fig. 4.The average grain size were calculated and found in between 1.2 -3.8 μm .The EDX examinations for random spots in the same sample confirmed and are consistent with our XRD analysis see Table.2.

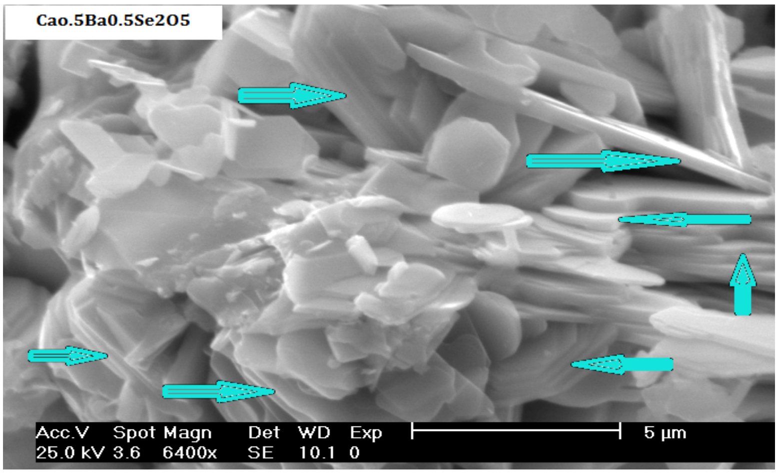

Fig.4 SE-micrograph captured for $Ca_{0.5}Ba_{0.5}Se_2O_5$ compound

From Fig.(4) it is so difficult to observe inhomogeneitiy within the same micrograph due to that the solution route synthesis with acetate-citrate precursors is yeilding to particle size might be in nano-range.The surface morphology can be described as two dimensional gray sheeth randomly ditributed as clear by black arrows in Fig.4 .

The grain size for $Ca_{0.5}Ba_{0.5}Se_2O_5$ compound was calculated according to " Scherrer's formula" [23 and 24],

$$B = 0.87\ \lambda/D \cos\theta \quad \ldots\ldots\ldots\ldots(1)$$

where D is the crystalline grain size in nm , θ,half of the diffraction angle in degree , λ is the wavelength of X-ray source (Cu-$K_\propto$) in nm ,and B,degree of widening of diffraction peak which is equal to the difference of full width at half maximum (FWHM)of the peak at the same diffraction angle between the measured sample and standard one.

Table.(2): EDX elemental data for $Ca_{0.5}Ba_{0.5}Se_2O_5$ compound

Element	Wt %	Average At %	K-Ratio	Z	A	F
O K	36.98	65.25	0.0329	1.1134	0.2831	1.0304
CaK	19.29	5.13	0.0179	1.1133	0.7753	1.0021
BaK	19.22	5.48	0.1731	1.0346	0.9807	1.1313
SeK	23.96	20.65	0.1513	0.8571	1.2118	1.1178

From SEM-maping, the estimated average grain size was found to be lower than those calculated applying Scherrer's formula for the same compounds . This indicates that the actual grain size in the material bulk is smaller than that detected on the surface morophology. Similar behavior of grains size calculations differences between bulk and material surface was recorded by many authors [25-27] that due to ambient processing temperature and applied experimental condition .

CONCLUSION

The conclusive remarks inside this article can be brief as:

[1] Acetate-citrate sol-gel route is successful technique for synthesis $Ca_{0.5}Ba_{0.5}Se_2O_5$**.**
[2] Barium-ions substitute successfully on the calcium sites of AB_2X_5 selenate type .
[3] The average grain size of $Ca_{0.5}Ba_{0.5}Se_2O_5$ was found to be in between 1.2 -3.8μm.
[4] The visualization investigations confirmed the experimental synthesis.

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