3. The minimum portion of M-PAAm for gelation of PAAm/M-PAAm mixture is successfully explained by the close packing lattice model.
4. Interpenetration occurs above C* or the CGC, where gels are made more readily and density is higher.

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Studies on Thermal Decomposition of Barium Titanyl Oxalate by Factor Analysis of X-Ray Diffraction Patterns

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Factor analysis was applied to study the thermal decomposition of barium titanyl oxalate (BTO) which is used as the precursor of barium titanate. BTO was synthesized in H_2O solvent and calcined at various temperatures. The X-ray diffraction patterns were obtained to make the data matrix of peak intensity vs. 2θ. Abstract factor analysis and target transformation factor analysis were applied to this data matrix. It has been found that the synthesized BTO consists of the crystals of $BaC_2O_4 \cdot 0.5H_2O$ and $BaC_2O_4 \cdot 2H_2O$ as well as the amorphous solid of TiO-oxalate. The results also indicate that the BTO was transformed via $BaCO_3$ to $BaTiO_3$ and Ba_2TiO_4 during the thermal decomposition.

Introduction

Factor analysis has been used in the analysis of multivariate data where a number of independently contributing factors are required.[1] This method was applied to determine the contributing substances in IR spectra,[2,3] mass spectra,[4] UV spectra[5] and liquid chromatogram[6] for mixtures of substances.

A much veritable information is obtained with dozens of parameters that could possibly affect an analysis of data. A typical example of this is seen in a lot of lines which it is possible to obtain from a scanned X-ray diffraction pattern of even simple substance. For many years, the method used to obtain the useful information has been to focus on 1-3 lines and the diffraction pattern is compared with patterns of known substances until a match is obtained. This is a univariate approach to analysis and require skilled technique for the correct match of an X-ray pattern. For this reason, multivariate analysis such as factor analysis must be applied to all pattern data (d values and intensities).

In the present investigation, abstract factor analysis (AFA)[7] and target transformation factor analysis (TTFA)[7-9] have been used to determine the number of factors and to verify individually the presence of the suspected components contributing to the X-ray diffraction patterns, which were obtained during calcination of barium titanyl oxalate (BTO) synthesized in H_2O solvent system. Thus, the results of AFA and TTFA have been used to study the thermal decomposition process of the BTO.

BTO is a precursor of barium titanate ($BaTiO_3$), which is one of perovskite-type ceramics and is of interest for the effect of the positive temperature coefficients of resistivity (PTCR). Clabaugh *et al.*[10] reported that a high purity barium titanate of nearly perfect stoichiometry could be prepared by precipitating barium titanyl oxalate ($BaTiO(C_2O_4)_2 \cdot 4H_2O$ (BTO)) and subsequently converting this material to barium titanate by calcination. Kudaka *et al.*[11] also reported the optimum conditions for the formation of BTO in more detail. For the preparation of BTO, they added the mixed solution of barium chloride and titanium tetrachloride to the aqueous solution of oxalic acid.

Yamamura *et al.*[12] employed a revised Clabaugh method to prepare BTO in which the ethanol solution of the oxalic acid was added to the mixed starting solution of $Ba(NO_3)_2$ and $TiO(NO_3)_2$. Although Yamamura *et al.* speculated that the composition of the crystalline precipitate was $BaTiO(C_2O_4)_2 \cdot 3H_2O$ based on the thermogravimetric data, a recent study by Fang and Lin[13] showed that the precipitate produced by Yamamura method is composed of cyrstalline barium nitrate and amorphous titanium oxalate. They also performed

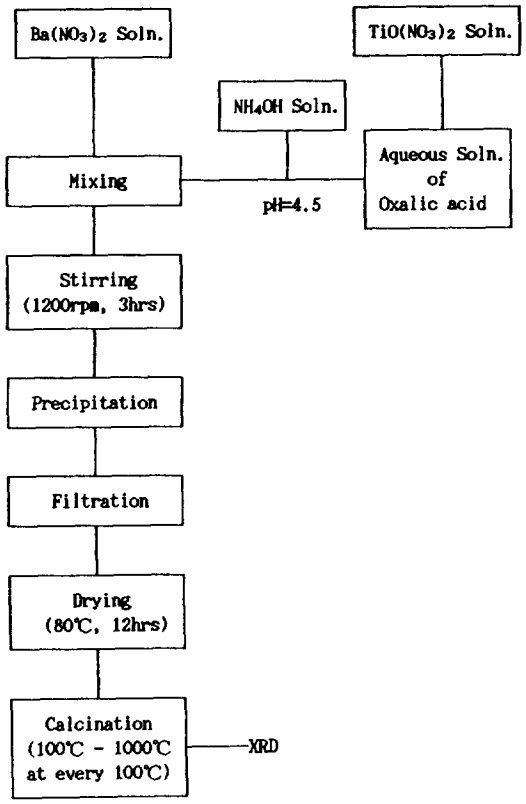

Figure 1. Flow diagram for the synthesis of $BaTiO_3$ in H_2O solvent system.

the thermogravimetric study to qualitatively evaluate the nature of the precursor and its mechanism of the thermal decomposition to barium titanate.

In this work the precursor was prepared in the H_2O solvent system using $Ba(NO_3)_2$ and $TiO(NO_3)_2$ as the starting materials. The precursor was converted to barium titanate by thermal decomposition. The thermal decomposition process was qualitatively estimated by factor analysis using X-ray diffraction patterns of the precursor.

Experimental

The flow diagram for the synthesis of the precursor is shown in Figure 1. The titanium solution has been stabilized by mixing with aqueous oxalic acid solution and adjusting to pH of 4.5 with ammonia solution. The barium solution was instantaneously added to the mixed solution. More detailed procedures are given elsewhere.[14]

The precursor was dried at temperature of 80℃ and divided into 10 portions. Each portion was heated in air at a rate of 15℃/min and held at a selected temperature in the range of 100-1000℃ for 2 hours. After cooling X-ray patterns of the samples were measured with X-ray diffractometer (XRD, Phillips PW 1710) by using Ni-filtered CuKα radiation. The X-ray diffraction patterns of some samples obtained at different temperatures are shown in Figure 2.

The diffraction patterns obtained at different firing temperatures were divided into 14 segments 5 degrees each. The measured intensities across each segment were summed. These give the reduced patterns of 14 integrated intensity

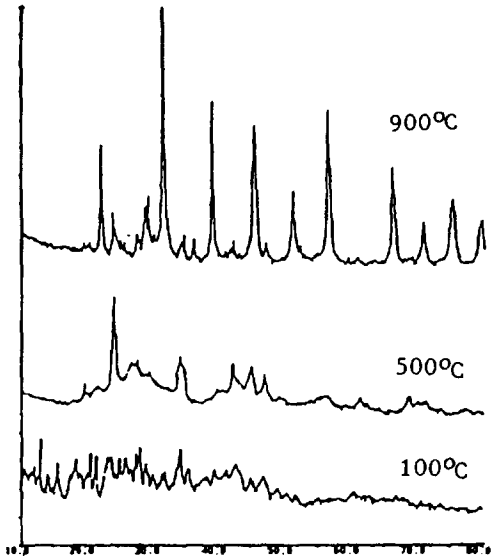

Figure 2. X-ray diffraction patterns.

Table 1. Data Set of Intensities at Various 2θ Values against Various Calcined Temperatures

2θ	100	200	300	400	500	600	700	800	900	1000
10-15	276	66	56	0	0	0	0	0	0	0
15-20	136	82	61	0	11	5	2	2	0	0
20-25	258	85	164	133	108	83	51	61	20	17
25-30	338	214	159	194	68	5	9	5	17	17
30-35	137	0	91	44	53	115	108	108	103	105
35-40	104	0	0	33	0	26	30	28	31	37
40-45	72	96	49	41	50	40	13	9	3	10
45-50	43	29	53	41	24	35	31	29	23	21
50-55	18	0	0	0	0	7	9	9	8	10
55-60	0	0	19	9	6	25	54	30	27	49
60-65	9	27	0	9	5	3	1	1	0	1
65-70	0	0	0	9	7	21	15	26	12	17
70-75	0	0	0	0	4	9	11	15	6	6
75-80	0	0	0	0	4	0	4	4	9	12

measurements. The reduced patterns are listed in Table 1. The standard XRD patterns of $BaCO_3$, $BaTiO_3$ and Ba_2TiO_4, etc., which are the suspected components in the samples, were chosen from the JCPDS (Joint Committee on Powder Diffraction Standards) data. The eight reduced standard patterns were similarly produced and are listed in Table 2.

Multivariate Analysis

Abstract Factor Analysis (AFA). The basis of this analytical technique is that the X-ray diffraction pattern of a mixture is equal to the weighted sum of the diffraction patterns of the individual components. That is, diffraction patterns may be represented by the array,

$$d_{ij} = \sum_{k=1}^{n} r_{ik} c_{kj} \quad (1)$$

where d_{ij} is the intensity at the ith reflection angle (2θ)

Table 2. Relative Intensities of Standards Obtained from JCPDS Cards at Various 2θ Values

2θ	$BaCO_3$	$BaTiO_3$	Ba_2TiO_4	BaC_2O_4	$BaC_2O_4 \cdot 0.5H_2O$	$BaC_2O_4 \cdot 2H_2O$	$BaTiO(C_2O_4)_2 \cdot 4H_2O$	$Ba(NO_3)_2$
10-15	0	0	0	0	148	32	204	0
15-20	13	0	8	120	140	153	390	100
20-25	153	37	41	240	185	57	281	49
25-30	19	0	391	240	250	69	397	10
30-35	61	100	117	150	109	135	0	30
35-40	6	46	113	180	108	26	0	120
40-45	73	12	134	240	138	76	0	13
45-50	20	37	83	150	82	32	0	22
50-55	8	21	197	50	32	22	0	19
55-60	12	50	60	0	30	14	0	25
60-65	7	0	52	0	18	18	0	10
65-70	14	22	44	0	0	10	0	23
70-75	10	12	28	0	0	0	0	6
75-80	4	24	0	0	0	0	0	11

in the jth mixture, n is the number of components in the mixture, r_{ik} is the intensity of the pure component k at the reflection angle $i(2\theta)$ and $c_{k,j}$ is the weighted concentration of the component k in the jth mixture. In matrix form, Eq. (1) becomes $[D]=[R][C]$. The problem of the analysis is to determine the $[R]$ and $[C]$ matrices.

AFA decomposes the data matrix into abstract factors. To accomplish this task, factor analysis (FA) makes use of the covariance matrix. The covariance matrix $[C_o]$ is calculated by $[D]\cdot[D]^T$, where $[D]^T$ is the transposed matrix of $[D]$. Throughout this work, the covariance about the origin has been used. The covariance matrix is then decomposed by the method of principal component analysis to produce the set of n principal eigenvectors $[K]$ and the corresponding eigenvalues λ.

$$[K]^{-1}[C_o][K]=\{\lambda_j\delta_{jk}\} \quad \delta_{jk}=0 \text{ if } j\neq k \qquad 1 \text{ if } j=k \tag{2}$$

Here δ_{jk} is the well-known Kronecker delta and λ_j is the eigenvalue of the set of equation having the following form

$$[C_o]\{K_j\}=\lambda_j\{K_j\} \tag{3}$$

where $\{K_j\}$ is the jth column of the matrix $[K]$. These columns form an orthonormal set.

In reality, the diagonalization matrix $[K]$ is a valid representation for the column matrix $[C]$, and the row matrix is given by Eq. (5).

$$[C]=[K]^T \tag{4}$$

$$[R]=[D][K] \tag{5}$$

The resulting matrices are abstract column and row matrices and are used to construct a linear model which can be used to reproduce the original raw data.

$$[D]=[R]_{abst}[C]_{abst} \tag{6}$$

The eigenvector analysis itself gives the number of components in an unknown mixture. There are numerous methods for determining the cut off between significant eigenvectors in total representing the number of components and the residual eigenvectors which represent random noise in the diffraction patterns.

The theory gives three types of errors,[7] *i.e.*, real error (RE), extracted error (XE) and imbedded error (IE). The errors are estimated according to Eq. (7)-(9).

$$RE=\left[\sum_{j=n+1}^{x}\lambda_j/y(x-n)\right]^{1/2} \tag{7}$$

$$XE=\left[\sum_{j=n+1}^{x}\lambda_j/yx\right]^{1/2} \tag{8}$$

$$IE=[(RE)^2-(XE)^2]^{1/2} \tag{9}$$

where x is the number of rows or columns in $[D]$, whichever is smaller; y is the number of rows or columns whichever is larger; n presents the number of factors used to reproduce the data matrix; λ_j is the jth eigenvalue of the data matrix.

Among the error functions, the RE method depends upon an accurate estimate of the error. Since such information is not available in this work, the IE function has been used. By studying the behavior of the IE value as the function of n, the size of the true factor space as well as the error in the data can be deduced without recourse to any a prior knowledge of the error. The point at which the IE value reaches a minimum corresponds to the true factor space.

IND function, an empirical function in nature as shown in Eq. (10), is given by Malinowski[7] to reach a minimum when the correct number of factors are employed

$$IND=RE/(x-n)^2 \tag{10}$$

The remaining n eigenvectors, also called abstract factors, span the same space spanned by real factors, *i.e.*, the components in the mixture. The data matrix $[D]$ can be reproduced by postmultipling the matrix comprised of the first n columns of the matrix $[R]$ by the first n rows of the matrix $[C]$. This can mathematically be shown as $[D]=[R]_{abst}[C]_{abst}$.

Target Transformation Factor Analysis (TTFA). A coordinate transformation from the abstract space to a real factor space is desired. The transformation as well as the identification of one or more of the factors present involve target testing of the suspected factors using the abstract row

Table 3. Results of Abstract Factor Analysis of Intensity Data Obtained from 100-1000℃

n	Eigenvalues	Cumulative(%)	RE	XE	IE	IND
1	524548.7	82.1	30.9	28.6	9.5	0.371
2	72953.6	93.6	19.2	17.1	8.6	0.299
3	26274.7	97.7	12.3	10.3	6.7	0.251
4	6857.7	98.7	9.8	7.6	6.2	0.271
5	5626.0	99.6	5.8	4.1	4.1	0.233
6	1556.5	99.9	3.8	2.4	3.0	0.238
7	466.8	100	2.9	1.6	2.4	0.319
8	224.9	100	2.1	0.9	1.9	0.522
9	104.5	100	1.1	0.4	1.1	1.125
10	17.7	100				

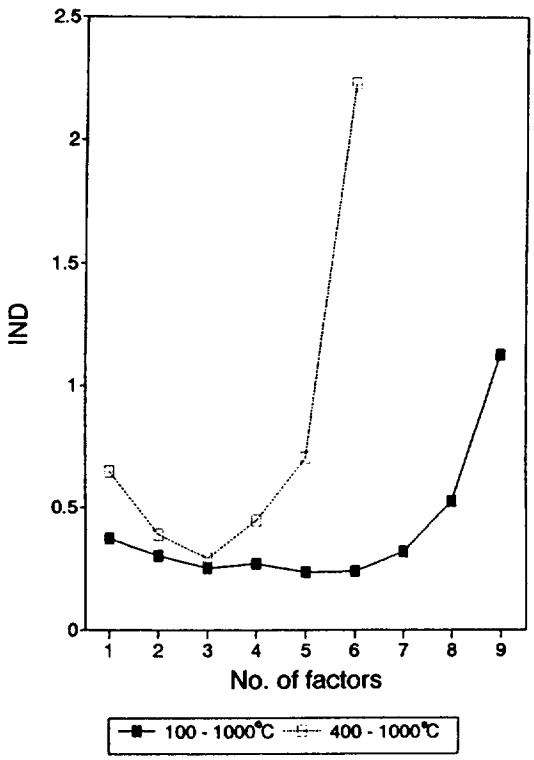

Figure 3. Plots of IND(indicator function) values.

matrix.[9] The suspected factors are represented by a test matrix $[\bar{\bar{R}}_f]$. The test matrix is constructed, which contains the known diffraction pattern of the standards and has the dimensions of $x \times n$, where x is the number of segments used to reproduce $[D]$ and n is the number of compoents determined.

The transformation matrix $[T_f]$ is written by Eq. (11)

$$[T_f]=[\lambda]^{-1}[R]^T_{abst}[\bar{\bar{R}}_f]$$
$$=[[R]^T_{abst}[R]_{abst}]^{-1}[R]^T_{abst}[\bar{\bar{R}}_f] \quad (11)$$

where $[R]^T_{abst}$ is the transposed matrix of $[R]_{abst}$. The transformation matrix can be used to calculate the predicted intensities and the predicted concentration according to Eq. (12) and (13), respectively.

$$[\bar{R}]=[R]_{abst}[T_f] \quad (12)$$

Table 4. Results of Target Testing for the Samples Obtained from 100-1000℃ Using Intensity Data of 8 Suspected Compounds

Compounds	AET	REP	RET	SPOIL
$BaCO_3$	13.42	6.58	11.70	1.78
$BaTiO_3$	8.05	3.06	7.45	2.43
Ba_2TiO_4	51.31	18.65	47.80	2.56
BaC_2O_4	58.58	7.73	58.07	7.51
$BaC_2O_4 \cdot 0.5H_2O$	21.82	6.07	20.96	3.45
$BaC_2O_4 \cdot 2H_2O$	22.55	9.51	20.45	2.15
$BaTiO(C_2O_4)_2 \cdot 4H_2O$	68.87	10.06	68.13	6.77
$Ba(NO_3)_2$	36.58	2.62	36.49	13.91

$$[\bar{C}]=[T_f]^{-1}[C]_{abst}=[T_f]^{-1}[K]^T \quad (13)$$

Results and Discussion

A 14-row by 10-column data matrix $[D]$ listed in Table 1 was formed from the intensities at 14 segments of 10 samples, which were fired at different temperatures. This matrix (14×10) was subjected to AFA. The theory of errors for AFA was applied in order to determine the number of factors n, *i.e.*, the number of components. This involved evaluating the RE, the IE and the IND by means of Eq. (7) to (10), using $n=1$ to $n=9$ factors to reproduce the data. Only the numbers of rows and columns in the data matrix, the eigenvalues and n were needed to these quanities. The AFA results for the 14×10 data matrix are given in Table 3.

The RE method depends upon an accurate estimate of the experimental error. Such information is not available in the present work. Therefore, the IE and the IND were used. The presence of three or five factors is indicated by the IE, since this value did not decrease appreciably beyond $n=3$ or $n=5$. The IND value also shown in Figure 3 reached a minimum at $n=3$ and $n=5$. The RE values at the $n=3$ and $n=5$ are 12.3 and 5.8 cps, respectively. The RE value at the $n=5$ was in accord with other study,[15] which reported the RE value of about 6 cps. And Fang and Lin[13] are also reported that the five components were formed in the thermal decomposition process. Therefore, the five suspected components were contained in the data matrix (14×10) of intensities.

After the number of factors was determined by AFA, target tests were individually carried out for the suspected components. Pure compositional patterns of standards given in Table 2 were used as the suspected components, *i.e.*, the target test vectors. The theory of errors for TTFA was applied to the eight target tests. The AET, RET and SPOIL values which were defined by Malinowski[7] have been calculated and are listed in Table 4. The value of the SPOIL is especially useful. According to Malinowski, a value of 0-3 indicates the test vector is a factor, 3-6 indicates it may be a factor, and values above 6 indicate that it is not a factor. The components of $BaCO_3$, $BaTiO_3$, Ba_2TiO_4, $BaC_2O_4 \cdot 0.5H_2O$ and $BaC_2O_4 \cdot 2H_2O$ known to exist in the data matrix succeeded with a value of the SPOIL near 3. The three components such as BaC_2O_4, $BaTiO(C_2O_4)_2 \cdot 4H_2O$ and $Ba(NO_3)_2$ had the SPOIL value of above 6 and therefore were not factors.

Table 5. Results of Abstract Factor Analysis of Intensity Data Obtained from 400-1000℃

n	Eigenvalues	Cumulative(%)	RE	XE	IE	IND
1	132581.7	74.3	23.3	21.6	8.8	0.648
2	39133.2	96.3	9.7	8.2	5.2	0.390
3	5437.3	99.3	4.6	3.5	3.0	0.290
4	535.1	99.6	4.0	2.6	3.0	0.443
5	445.0	99.9	2.8	1.5	2.4	0.705
6	153.0	100	2.2	0.8	2.1	2.232
7	69.8	100				

Table 6. Results of Target Testing for the Samples Obtained from 400-1000℃ Using Intensity Data of 8 Suspected Compounds

Compounds	AET	REP	RET	SPOIL
$BaCO_3$	7.93	6.51	4.53	0.70
$BaTiO_3$	8.21	2.38	7.86	3.31
Ba_2TiO_4	66.07	13.97	64.58	4.62
BaC_2O_4	63.77	6.85	63.40	9.26
$BaC_2O_4 \cdot 0.5H_2O$	59.70	5.54	59.44	10.73
$BaC_2O_4 \cdot 2H_2O$	44.57	2.47	44.50	18.02
$BaTiO(C_2O_4)_2 \cdot 4H_2O$	120.53	9.05	120.19	13.29
$Ba(NO_3)_2$	39.43	1.39	39.40	28.31

On the one hand, AFA was also applied to the diffraction patterns of samples which were obtained at a range of 400-1000℃. The X-ray diffraction of the samples shows the crystalline patterns. AFA results for the 14×7 data matrix are listed in Table 5. The IE and IND values indicated that the three factors were contained in the data matrix (see Figure 3). The results of the target testing of the eight suspected factors given in Table 2 are listed in Table 6. The three $BaCO_3$, $BaTiO_3$ and Ba_2TiO_4 components were found to have the SPOIL value of below 6.

The results of factor analysis for the two matrices (14×10 and 14×7) indicate that the samples obtained at a range of 100-1000℃ containe the five $BaCO_3$, $BaTiO_3$, Ba_2TiO_4, $BaC_2O_4 \cdot 0.5H_2O$ and $BaC_2O_4 \cdot 2H_2O$ crystalline compounds, and the samples obtained at a range of 400-1000℃ containe the three $BaCO_3$, $BaTiO_3$ and Ba_2TiO_4 crystalline compounds. Therefore, the samples obtained at a range of 100-300℃ containe the crystalline compounds of $BaC_2O_4 \cdot 0.5H_2O$ and $BaC_2O_4 \cdot 2H_2O$. Fang and Lin reported that $BaC_2O_4 \cdot 0.5H_2O$ and α-BaC_2O_4 were formed below 350℃ by the thermal decomposition of BTO. The BTO was prepared by addition of the mixed solution of barium chloride and titanium tetrachloride to aqueous solution of oxalic acid at pH=7. The formation of $BaC_2O_4 \cdot 2H_2O$ instead of α-BaC_2O_4 might be due to the difference in titration methods as well as the difference of pH for synthesizing BTO.

In conclusion, the BTO obtained at <400℃ consists of the crystal solids of the $BaC_2O_4 \cdot 0.5H_2O$ and $BaC_2O_4 \cdot 2H_2O$ as barium component as well as the amorphous solid of TiO-oxalate as titanium component. And the X-ray patterns of samples obtained at >400℃ contain crystalline compounds of $BaCO_3$, $BaTiO_3$ and Ba_2TiO_4. It seems that the crystalline compounds of $BaC_2O_4 \cdot 5H_2O$ and $BaC_2O_4 \cdot 2H_2O$ were transformed to $BaCO_3$, $BaTiO_3$ and Ba_2TiO_4 during the thermal decomposition. The factor analysis of the X-ray diffraction patterns could be used to determine intermediates instead of conventional thermogravimetric method.

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